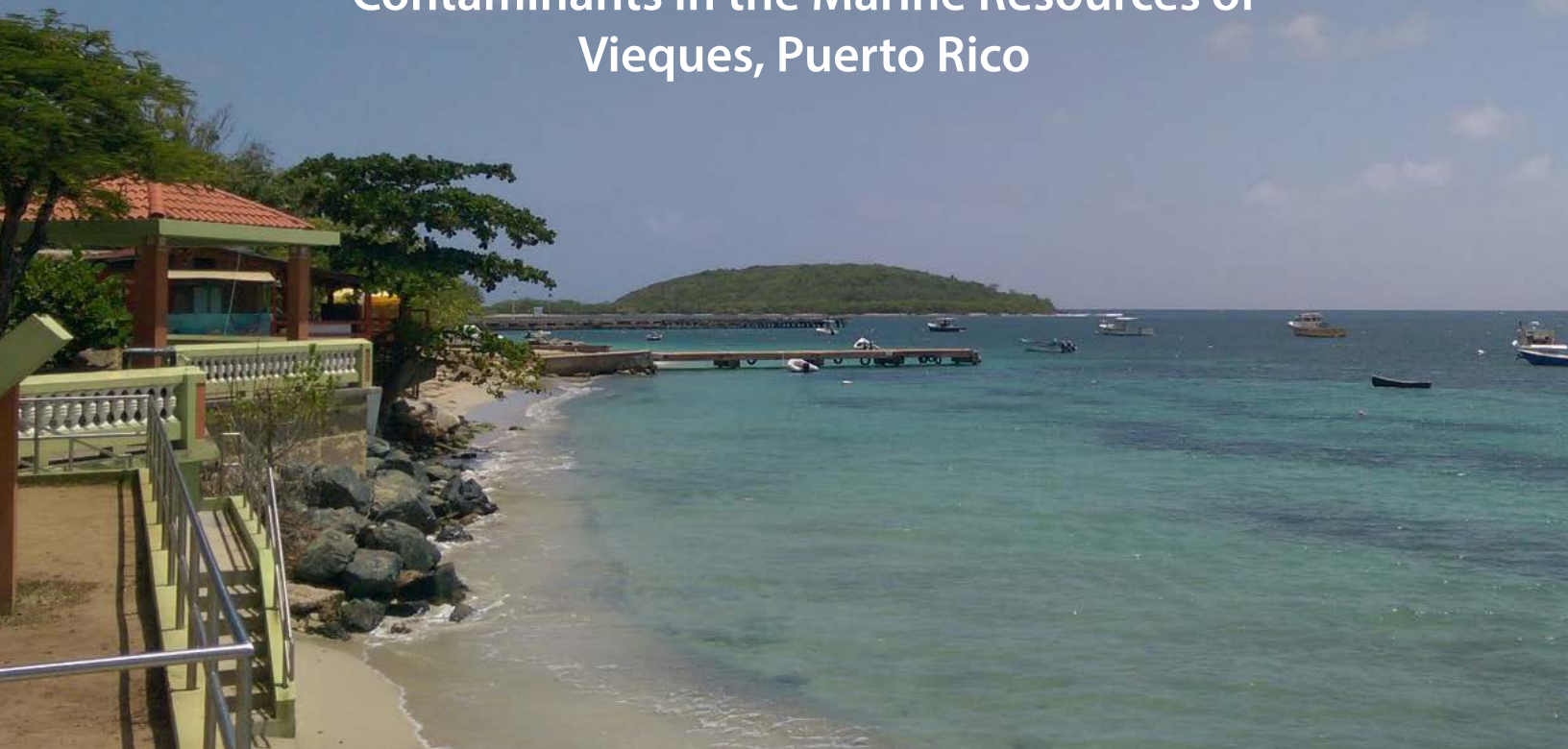


# Contaminants in the Marine Resources of Vieques, Puerto Rico



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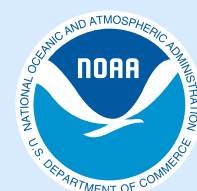
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September 2016

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# Chemical Contaminants in the Marine Resources of Viques, Puerto Rico

September 2016

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NOAA Technical Memorandum NOS NCCOS 223

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## **ABOUT THIS DOCUMENT**

This document represents a study carried out at the request of the Puerto Rico Department of Natural and Environmental Resources (PRDNER).

The report details the concentrations of metals, the pesticide DDT (and its degradation products) and energetic compounds (associated with munitions) in conch and lobster in Vieques, Puerto Rico.

The efforts discussed here were led by the National Centers for Coastal Ocean Science (NCCOS), the Office of Response and Restoration and NOAA's Coral Reef Conservation Program (CRCP), with significant participation from partners, such as Puerto Rico DNER and the U.S. Fish and Wildlife Service. NCCOS has been proactive in collaborating with other NOAA offices as well as federal, state and non-governmental organization partners to maximize cost-sharing efforts and reach its goals.

Their efforts and extramural funding has made it possible to complete assessments that would have otherwise been unobtainable through federal funding alone.

Live hyperlinks to related products (indicated by blue text) are embedded throughout this report and are accessible when viewing this document as a PDF. For more information about this report and others like it, please visit the NCCOS web site, <http://coastalscience.noaa.gov/>, or direct comments to:

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## EXECUTIVE SUMMARY

Pollution in the marine environment has the potential to negatively impact ecosystem health, including adverse effects on fisheries species. This can occur through direct impacts, food web effects and habitat degradation. Vieques is an island municipality of the Commonwealth of Puerto Rico, located 11 km off the east coast of the main island. In addition to normal pollution stressors associated with human activities, Vieques was also the site of a military bombing range from the 1940s until 2003. Local concern exists about potential impacts of pollution from these and other activities on fisheries stocks, as well as potential seafood safety issues. In this study, queen conch (*Strombus gigas*) and spiny lobster (*Panulirus argus*) tissues were analyzed for a suite of contaminants: metals, the pesticide DDT (and its degradation products), and energetic compounds (associated with munitions) from three areas around the island. Concentrations of pollutants in queen conch were compared to other published values for the region, and compared with conservative seafood safety guidelines.

Key findings from this study include:

- Munitions compounds were not detected in any samples in this study.
- Degradations products of DDT (a legacy pesticide) were only detected in one conch sample and at relatively low levels. The parent material (DDT) was not detected in any samples.
- There was no clear spatial pattern in conch data on the island that might indicate a pollution “hot spot.” Each sampling area, including the “less impacted” comparison site, had at least one analyte that was higher than the other areas.
- Concentrations of metals measured in queen conch were within the range of values reported in other studies in the Caribbean, suggesting that pollution levels in conch in Vieques are not unusual for the region.
- Although not the purpose of this study, very conservative indigenous fish consumption guidelines (EPA; sixteen 8 ounce meals per month) were exceeded by samples in this study. However, based on other published studies these measured concentrations in Vieques are not unusual for the larger Caribbean region.
- Limited lobster data (n=2) prevented a rigorous analysis of for this species.



## CHAPTER 1: INTRODUCTION

Vieques is an island municipality of the Commonwealth of Puerto Rico that is located 11 km southeast of the main island of Puerto Rico. The island is approximately 33 km long and 7 km wide, with a land area of 127 km<sup>2</sup>. The island and surrounding waters are characterized by a diversity of terrestrial, estuarine, and marine habitats. The municipality includes two towns located on opposite sides of the mid-section of the island, Isabel Segunda on the north shore and Esperanza on the south coast (Figure 1). The 2010 Census estimated the population of Vieques at 9,301 (U.S. Census 2016).

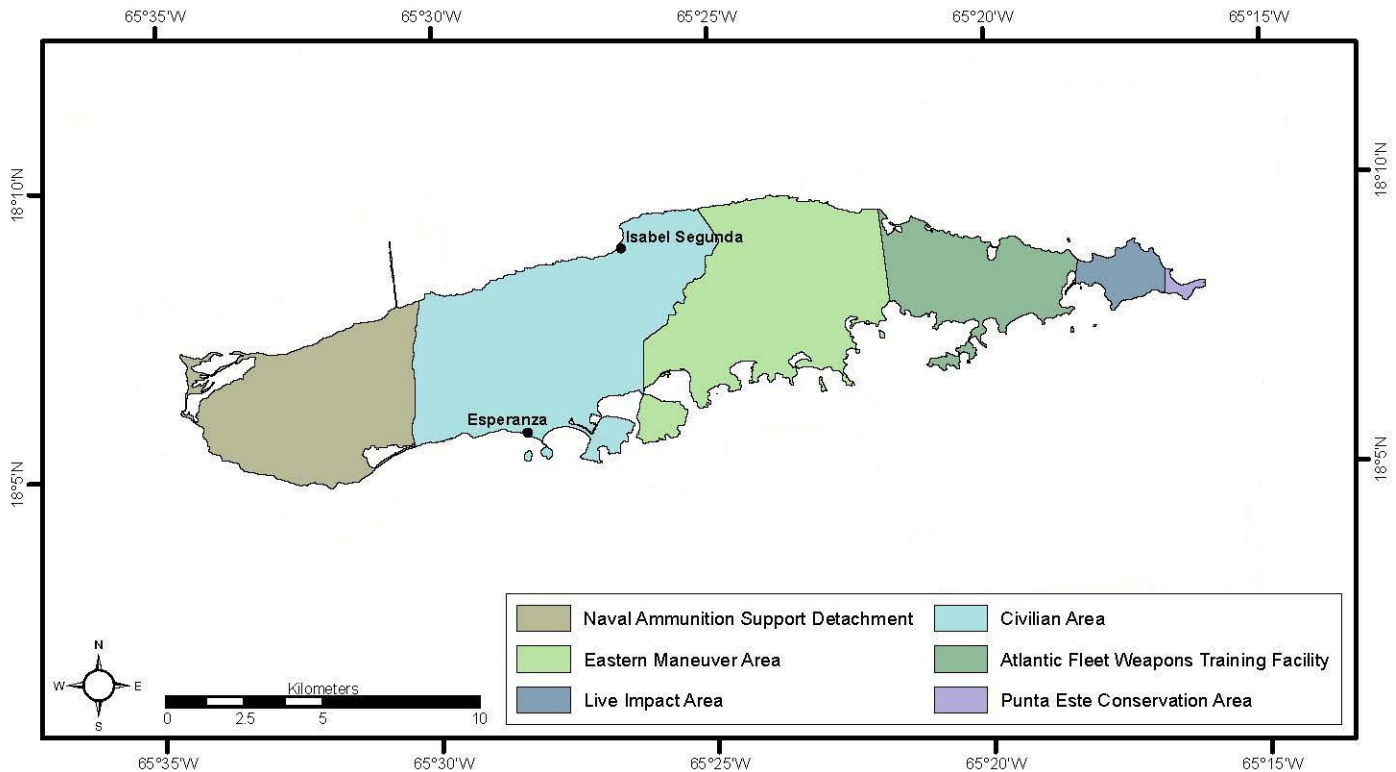


Figure 1: Historical land use (1941 to 2003) of Vieques. Adapted from Bauer et al. 2008. Inset map shows location of Vieques in relation to mainland Puerto Rico.

The current and historic land use on Vieques affects the distribution and condition of the marine resources of the island. The island's landscape has undergone various stages of human development dating from the first human habitation (ca. 200 BC, Langhorne 1987). Until the 1800s, Vieques was inhabited by native tribes and later by a variety of European (Spanish, English, Dutch, French) settlers (Langhorne 1987). Under Spanish rule, much of the land was cleared for sugar cane and timber harvesting, to the detriment of native forests. Along with the rest of Puerto Rico, Vieques became part of the the United States in 1898 following the Spanish-American War. The sugar industry prospered into the early 20th century, but began a gradual decline in the 1920s and 30s.

Between 1941 and 1947, the United States government annexed approximately two-thirds of the land on Vieques for use by the Navy as a training facility (Figure 1). At the time of acquisition by the U.S. Navy, sugar was no longer a viable industry (Langhorne 1987). The Naval Ammunition Support Detachment (NASD), located on the west end of the island, was used primarily for ammunition storage. The municipality of Vieques, including the towns of Isabel Segunda and Esperanza, lay between the NASD and eastern Navy zones. The eastern half of the island consisted of lands used for training activities

including air, sea, and maneuver warfare, air-to-ground bombing, amphibious landings, and artillery training operations. Bombing activities were primarily localized within the Live Impact Area (LIA) and adjacent waters. Locations of amphibious assault training activities included: Punta Arenas (Green Beach), Playa Matia (Yellow Beach), Playa Chiva (Blue Beach), Playa Caracas (Red Beach), and Playa Campana (Purple Beach). Detailed information about prior Naval activities in Vieques can be found in a number of sources (DON 1979; DON 1986; DON 2001; GMI 2003; CH2M HILL 2004; GMI 2005). In 2001, the Navy began decreasing their activities and the process of transferring land ownership began. Naval training activities ceased in 2003. In 2001, 17 km<sup>2</sup> of former Navy lands on western Vieques were transferred to the municipality, 3.2 km<sup>2</sup> to the Puerto Rico Conservation Trust (<http://www.fideicomiso.org>), and 12.5 km<sup>2</sup> to the Department of the Interior (DOI 2007). The Navy retained a small parcel of land on the southwestern portion of the island for its Relocatable Over the Horizon Radar (ROTHR) facility. In 2003, the eastern Navy lands were also transferred to the Department of the Interior. The lands under jurisdiction of the DOI's Fish and Wildlife Service make up the Vieques National Wildlife Refuge (DOI 2007). It should be noted that the beaches, wetlands, offshore island and cays fall under the jurisdiction of the Commonwealth of Puerto Rico. In 2005, the former Navy areas of Vieques were added to the National Priorities List (NPL or "Superfund"), legislation which requires the Navy to undertake activities needed to identify and clean-up contaminated areas by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Federal Register 7182-7189 2005). Through this program, the Navy is currently removing terrestrial unexploded ordnance (UXO), which often necessitates open detonation or "blow-in-place" of unexploded ordnance. Public access is currently restricted in a large part of the eastern refuge lands due to these activities and other remnant hazards. At the time of this publication, clean up was ongoing and was expected to take until at least 2025.

A NOAA field study of Vieques in 2007 (Bauer et al. 2009) examined the biology and pollutant stressors of the marine resources of the island. Hard bottom benthic habitat was found to account for two thirds of the total area, but live coral cover was less than 10% for 93% of the mapped area. Turf algae represented

the most common benthic cover type. Fish communities consisted of 34 taxonomic families and 110 species with individuals from the families Labridae (wrasses) and Pomacentridae (damselfishes) being the most numerically abundant. Surgeonfishes (Family Acanthuridae) and parrotfishes (Family Scaridae) accounted for the highest proportion of biomass. Differences in fish and benthic communities among strata could not be



*Image 1: Ensenada Honda from the water (looking northwest).*

conclusively linked to former land-use patterns. Vieques is similar in terms of benthic cover, total fish abundance and biomass to other nearby locations in Southwest Puerto Rico, St. Croix, and St. John in the USVI. This study also quantified a broad suite of contaminants in sediments and coral tissues. It found that, in general, contamination in the marine environment of Vieques was relatively low. Exceptions were DDT (at four sites) and chromium (at one site) which were detected above sediment quality guidelines. No munitions compounds were detected in the marine environment. Similarly, other studies (ATSDR 2003, ATSDR 2013, CH2MHill 2015) have not found widespread contamination in the marine environment.

However, public concern still exists about the role of former land use activities on the marine health of the island, including fish harvests and seafood safety. In 2013, fishermen and other local activists voiced concerns that pollution coming from an inland lagoon (Laguna Anones) near the LIA was reaching the coastal ocean and has led to decreased fish harvests (Primera Hora, 2013).

In order to address these concerns, this study, completed at the request of the Puerto Rico Department of Natural and Environmental Resources (PRDNER), had the following primary objectives:

- Quantify contaminant levels in species important to the Vieques fishery.
- Determine spatial differences within the study area.
- Put findings in a larger context using information available in the scientific literature.



*Image 2: Bahia Salinas del Sur from the water (looking north).*

In April of 2014, scientists from NOAA and the Puerto Rico Department of Natural and Environmental Resources (DNER) consulted with the local fishing community to determine fishing areas of concern near the island. Federal resource managers (US Fish and Wildlife Service and US Environmental Protection Agency) were also consulted. Two areas on the south shore of island were identified as being of concern: Ensenada Honda and Bahia Salinas del Sur (Figure 2). Bahia Salinas del Sur is located adjacent to the former LIA, where most of the live bombing occurred.

Ensenada Honda, while not in the LIA, is adjacent to, and downstream from (based on the prevailing longshore current) the restricted area where military activities occurred. Additionally, the fishermen identified an area on the north shore, near Mosquito Pier, that they felt was relatively less impacted by pollution. While this “unimpacted” site is not a true control, it is useful for comparative purposes, as it is far less likely to have been affected by bombing activities.



Two null hypotheses are relevant to these objectives. The first null hypothesis is that there are no differences between the east end of the island and the northwest end of the island; rejection of this null hypothesis might be expected if military activities on the east end of the island had negatively impacted biota. A second null hypothesis is that there are no differences between Vieques and other ecosystems in the region; rejection of this null hypothesis would indicate that Vieques might have higher (or lower) levels of pollution than the rest of the region.

### Species Selection

From a list of species that were identified by the community as important to the fishery, three species were selected for contaminant analyses: queen conch (*Strombus gigas*), Caribbean spiny lobster (*Panulirus argus*), and red hind grouper (*Epinephelus guttatus*). These species were selected from a larger list suggested by the fishermen using criteria including: habitat range, the extent to which the organism is exposed to the benthos (i.e. a likely source of pollution), and potential for bioaccumulation.



Image 3: Scientific divers in the waters of Vieques to sample conch and lobster.

Queen conch habitat and feeding mechanisms are well suited to examining contamination. Queen conch are large marine soft bodied gastropod mollusks with a hard calcium carbonate shell. They are found throughout the tropical western Atlantic (Martin, 1995), generally in waters between 5 and 20 m, with their depth range being limited primarily by food sources (Sterrer, 1986). The habitat includes coral reefs, rocky shores, sea-grass beds and patchy sand flats (Randall, 1964). Queen conch feed on plant material (e.g. *Thalassia*), epiphytes and benthic algae, and may ingest sediment particles during this process (Randall, 1964). Conch can live up to 30 years (McCarthy, 2008) and reach up to 30 cm in length (Randall, 1964). Individuals reach sexual maturity at 3–4 years of age (McCarthy, 2008) and are especially susceptible to predation as juveniles, i.e. prior to shell formation (Appeldoorn and Mason, 2013). Queen conch have relatively small home ranges (mean of 6 ha, Glazer et al., 2003). This small home range, in combination with its benthic habitat, make conch well suited for contaminant studies. Conch is an important food source across the Caribbean. Pollution has been shown to be correlated with negative impacts in queen conch populations (Glazer et al., 2008; Spade et al., 2013).

The geographic range of the spiny lobster (*Panulirus argus*) includes tropical and subtropical waters of the Atlantic Ocean from North Carolina to Brazil, including the Caribbean Sea and the Gulf of Mexico (Marx and Herrnkind 1986). Habitat depths range from low tide to about 90 meters (Sterrer 1986). Spiny lobsters generally forage at night, feeding on bivalves, chiton, gastropods, small mollusks, small

crustaceans and echinoderms, as well as carrion. Coral reef crevices and overhangs function as daytime refuge. Although the adult lobsters live on the reef, earlier life stages can be found in macroalgae beds. Seagrass beds function as nurseries for this species (Marx and Herrnkind 1986). *Panulirus argus* is both a sport and commercial species. Its benthic habitat and feeding habits, combined with its small home range, make it well suited for contaminant studies.

The red hind grouper (*Epinephelus guttatus*) is an ecologically and commercially important grouper (Heemstra & Randall 1993, Coleman et al. 2000). Red hinds make up a large proportion of recreational and fisheries catches throughout the Caribbean (Burnett-Herkes 1975, Heemstra & Randall 1993). This reef fish has a relatively small home range (when compared to other harvested fish species) making it a good candidate for contaminant studies (Pittman et al. 2014)

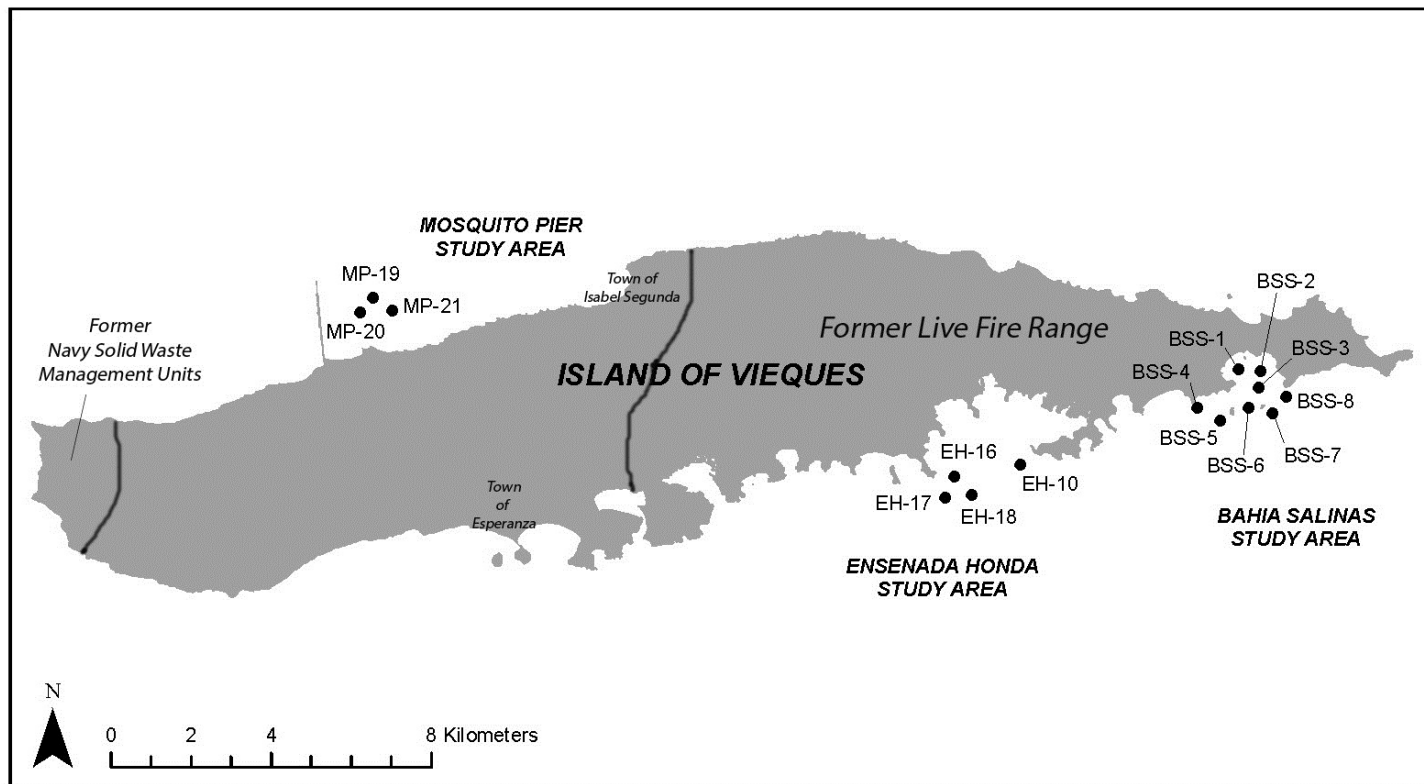


Figure 2: Site map with labels. MP=Mosquito Pier, EH=Ensenada Honda, BSS=Bahia Salinas del Sur.

## Materials and Methods

### Sampling Design

The sampling design called for three individuals of each species to be collected from each sampling area (21 individuals of each species; 63 total organisms, see Figure 2). Sampling polygons were delineated based on the areas identified by fishermen, and using benthic habitat maps. The two larger areas (Ensenada Honda and Bahia Salinas del Sur) were subdivided into three sub-strata in order to ensure that fishing effort was being applied across the entire strata (Figure 2). Each polygon was constructed so that it contained both reef and seagrass habitat, in order to accommodate primary habitats of the target species.

### Sample Collection Methods

The strata were navigated to on a small boat using handheld GPS. Due to vessel limitations, sampling was limited to daylight hours (approximately 7 am to 5 pm). Sampling occurred the week of August 10th, 2014. Using search and rescue swimming patterns, divers searched the benthic habitat within



*Image 4: Hook and line fishing for grouper in Vieques.*

each of the sampling sub-areas, looking for live conch of legal harvest size (>9 inches in total length) and lobster of legal harvest size (carapace length of >3.5 inches). The total number of conch collected was limited to 15 because it was difficult to find conch large enough for legal extraction. Only three lobsters of legal size were observed, two of which were collected (one escaped capture). Red hind grouper were targeted using hook and line fishing, via a variety of baits (shrimp, squid, whelk) presented near the reef (i.e. bottom fishing). Hook and line fishing was employed because fish traps could not be used due to the widespread presence of unex-

ploded ordnance, and spearfishing can lead to the loss of bodily fluids (i.e. from the puncture wound) that could bias the analysis. Unfortunately, no red hind grouper were collected during the field mission, although divers did observe some grouper in the study area. This may have been due to the fishing method, the time of day (which was limited by boat availability) or by species abundance.

Nitrile gloves were worn during collection and handling to reduce the potential for between-site contamination. Once aboard the boat, individual conch were placed in sealed plastic freezer bags and stored on ice. Individual lobsters were wrapped in aluminum foil, placed in bags and stored on ice. At the end of each field day, samples were frozen (-20° C). After freezing for at least 24 hours, conch were partially thawed on ice which allowed the tissue to be extracted from the shell whole. The extracted conch tissue was then placed in pre-cleaned HDPE containers and re-frozen. Lobsters were shipped whole. Samples were sent via overnight shipment to the NOAA analytical lab (Center for Coastal Environmental Health and Biomolecular Research) in Charleston, SC.

Conch and lobster tissue samples were analyzed for a suite of analytes (Table 1) including: munitions compounds, metals and DDT (and its degradation products). DDT is reported as total DDT (sum of parent material and degradation products) for simplicity. Unless otherwise noted, metals are reported as total concentrations.

#### Laboratory Methods

Conch and lobster were received at the laboratory in Charleston, SC and stored at -40°C prior to preparation for analysis. Briefly, tissues were prepared after thawing by homogenizing each conch in a Teflon container using a titanium handheld probe homogenizer (ProScientific, Inc.). Only the commonly consumed lobster tissue (tail meat) was homogenized for analysis. Homogenized samples were sub-sampled for organic contaminant analysis (munitions, DDTs) and trace metals analysis (Balthis et al., 2012). Moisture content was determined by weighing before and after drying in an oven at 85°C (>24 hr) until constant mass was achieved. All data were validated by comparison with blanks, spikes (matrix and reagent spikes), and certified reference materials.



Trace metal determination used methods described in Reed et al. (2015). Briefly, homogenized tissue was microwave-digested in nitric acid followed by peroxide addition. Analysis for 21 elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb, Se, Sn, Ti, U, V, and Zn) was achieved using ICP-MS (Perkin Elmer Elan 6100), while Hg was determined by direct mercury analysis (DMA-80, Milestone Inc.).



*Image 5: Queen conch sampled on south shore of Vieques.*

DDTs were determined by GC/MS (Kimbrough et al, 2006) with slight modifications to the protocols. Briefly, samples were prepared for accelerated solvent extraction (ASE) by grinding the sample homogenate with ~28 g anhydrous sodium sulfate in a mortar. Internal standards were added to the samples prior to extraction by ASE. Post-extraction cleanup was achieved using gel permeation chromatography, and collected fractions were further processed using activated alumina. Final extracts were analyzed using an Agilent 6890 gas chromatograph paired with an Agilent 5973 mass spectrometer.

The determination of munitions compounds in marine tissues was achieved by two separate extraction methods (Table 2), a modification of EPA 8330B (USEPA 2006) and a Dionex ASE 200. Samples were extracted by both methods.

In the modified EPA 8330B method, homogenized sample aliquots (~10 g wet) were lyophilized in amber vials for two days prior for water removal. After lyophilization, samples were transferred to hexane-rinsed mortar bowls and ground into a fine powder. Samples were returned to their respective vials and stored in a foil-covered desiccator until extraction. Tissues samples of ~1.2 g dry (corresponding to ~4.5 g wet) were placed into solvent-rinsed, 50 ml glass centrifuge tubes. The internal standards 13C7, 15N3-TNT, 13C4, 15N4-HMX, 13C3-RDX, d5-nitrobenzene and 3,4-dinitrotoluene were added followed by 15 mL of 50:50 dichloromethane/acetone. Centrifuge tubes were capped and vortexed for 1 minute, then placed into a chilled sonicator bath for 3 hours; temperature did not exceed 30°C.

For ASE, roughly 4.2 g of wet tissue sample was placed into a solvent rinsed mortar bowl containing ~27 g of anhydrous sodium sulfate. Samples were ground thoroughly and transferred into 33 mL ASE cells. Samples were spiked with the internal standards and extracted using an ASE 200 using a 50:50 dichloromethane/acetone mixture at 1000 psi. Calibration standards, reagent spikes, and matrix spikes were extracted by ASE in addition to the samples (range: 10-250 ng).

After extraction (sonication or ASE) samples were filtered through sodium sulfate into 200 mL TurboVap tubes and concentrated under a stream of nitrogen (pressure did not exceed 1.1 bar, water bath temperature = 25°C). Samples were concentrated to 0.5 mL and solvent exchanged with dichloromethane once. Samples were again concentrated to 0.5 mL and were transferred to glass culture tubes. TurboVap tubes were rinsed three times with dichloromethane and added to the sample extracts (Fv=2 mL.) Samples were then cleaned up using a J2 Scientific gel permeation chromatography (GPC) system (J2 Scientific Biobead column with 100% dichloromethane as the mobile phase). After GPC cleanup, samples were concentrated to 0.5 mL and solvent exchanged to methanol twice. Extracts were concentrated to 0.5-1 mL and filtered through 0.45µm PTFE filters into amber sample vials. Recovery standards were added prior to instrumental analysis (1,2-dinitrobenzene and d4-17β estradiol).

Sample extracts were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) and gas chromatography mass spectrometry. GC/MS was used since several analytes would not ionize on the LC-MS/MS platform. While EPA methods use HPLC-DAD, initial work showed multiple interferences with conch and lobster tissue. For LC-MS/MS, an Agilent 1100 Series HPLC/AB Sciex API 4000 tandem mass spectrometer, operated in negative electrospray ionization with scheduled multiple reaction monitoring, was used. Separation was performed by a Phenomenex Synergi 4u Hydro-RP 80A column using a methanol/water gradient. For GC/MS analysis, an Agilent GC/MS (6890/5973N) operated in selected ion monitoring was used. Samples were injected onto a Restek DB-225ms column (30m x 0.25  $\mu$ m x 0.25 mm) through a split-splitless injector. Calibration curves (10-250 ng) were prepared for each batch of samples (from 8 to 13 samples). For ASE samples, the extracted curve was used, while sonication extracted samples used a calibration curve prepared directly from a stock solution.

All spiking/calibration and internal standard stocks were stored refrigerated (4° C) in glass amber bottles. Working stocks for spiking and calibration were volumetrically prepared weekly from concentrated stocks in methanol to minimize degradation. Standards for the native compounds were purchased from AccuStandard, while stable isotope-labeled standards were purchased from AccuStandard and Cambridge Isotope Laboratories.

### Statistical Methods

Data were analyzed using JMP statistical software. Because only two lobsters were collected, the data are shown in Appendix A, but no statistical analysis can be completed. Because the conch data were not normally distributed (Shapiro-Wilk test), non-parametric statistics (Wilcoxon with post-hoc Dunn's test,  $\alpha=0.05$ ) were used to evaluate differences between the sampling areas.

### Putting the Results in Context

Because data from the St. Thomas East End Reserve (STEER) were also generated by NOAA using similar methods, a statistical comparison was done on the raw data between the Vieques conch concentrations and those from the STEER. Data were first made comparable by converting the STEER data to a wet weight basis. Additionally, data from this study were also compared to queen conch data from previously published studies in Florida (Glazer et al. 2008) and Cuba (Rizo et al. 2010).

Although this study was not designed to evaluate conch from a seafood safety perspective, these data can be compared with previously published seafood consumption guidelines. In the interest of being as protective to public health as possible (i.e. conservative), the most stringent available guidelines were selected. These guidelines for sport and subsistence fishing (EPA, 2000) present acceptable tissue concentrations for varying levels of human consumption (i.e. 8 ounce meals per month). Data from the current study were compared to the highest published consumption rates (sixteen 8 ounce meals per month), meaning that the published acceptable tissue concentrations are very low. Guidelines do not exist for all measured analytes, only for DDT, arsenic, cadmium, mercury and selenium. Furthermore, these guidelines do not account for possible synergistic effects of multiple contaminants. In order to compare arsenic data from this study (total arsenic) to the guidelines (only inorganic arsenic is toxic), inorganic arsenic was assumed to make up 2% of the total arsenic in the conch tissue (EPA, 2012).

## Results and Discussion

Summary statistics for the chemical constituents quantified in queen conch in this study are shown in Table 3. Limited lobster data is shown in Appendix A. Each analyte, including background information on sources/uses, environmental impacts, analysis of spatial patterns, and comparison with other data, is discussed by pollutant group (e.g. DDT) or by individual analyte (e.g. metals). Because metals are naturally occurring in the environment, concentrations below the method detection limits are reported as the detection limit concentration, rather than as zero.

Sources of each analyte are discussed below and summarized in Table 4. It should be noted that metals are naturally occurring in the environment, so their mere presence does not indicate contamination. Furthermore, some metals (e.g. Fe, Cr, Cu) are essential micronutrients for a variety of plants and animals.

#### Munitions Compounds

Analysis for a suite of common munitions-related compounds (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), tetryl, nitrobenzene, 2,4,6-trinitrotoluene, 4-amino-2,6-dinitrotoluene, 2-amino-2,4-dinitrotoluene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, pentaerythritol tetranitrate (PETN), 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,2',6',6'-tetranitro-4,4'-azoxytoluene) resulted in no concentrations above the method detection limit. The absence of munitions constituents in conch tissues is consistent with previous studies of marine sediments (Pait et al. 2010), which also did not detect these compounds in the marine environment of Vieques. While there is no debate that munitions were used in large quantities on Vieques, these compounds do not seem to be prevalent in the coastal ecosystems. This is consistent with what has been reported at other former military sites (ATSDR 2007, Cox et al. 2007). Some data suggests that munitions compounds in marine environments are rapidly degraded by bacteria (Montgomery et al. 2008). Lotufo et al. 2013 concluded that ecological risks from munitions constituents in marine systems are negligible. These conclusions were based on the fact that munitions compounds are not considered to be bioaccumulative, because high elimination rates for these compounds resulted in an essentially complete loss of body residue within hours to days of when the source of contamination was removed. As such, aqueous exposure rather than dietary uptake is the dominant route of exposure.

## DDT

**Background:** Dichlorodiphenyltrichloroethane (DDT) is a hydrophobic, man-made organic chemical which was used historically as an organochlorine pesticide. In this study we present total DDT, which is the sum of DDT and its degradation products (DDMU, DDE and DDD).

**Uses:** DDT was widely used as an insecticide, both in agriculture and for mosquito control, until it was banned in the United States in 1972 due to environmental concerns.

**Environmental effects:** DDT is of concern due to its environmental persistence, potential to bioaccumulate, and toxicity to non-target organisms. These concerns led to its ban in the United States, but because of its persistence and heavy use in the past, residues of DDT can be found in the environment, including biota. DDT is still used in some parts of the world, especially for malaria control. DDTs act on biota as a neurotoxin and have been shown to be an endocrine disruptor. DDT and its metabolite DDE have been specifically linked to eggshell thinning in birds, particularly raptors (EPA 2009). DDT is also toxic to aquatic life including crayfish, shrimp and some species of fish (EPA 2009).



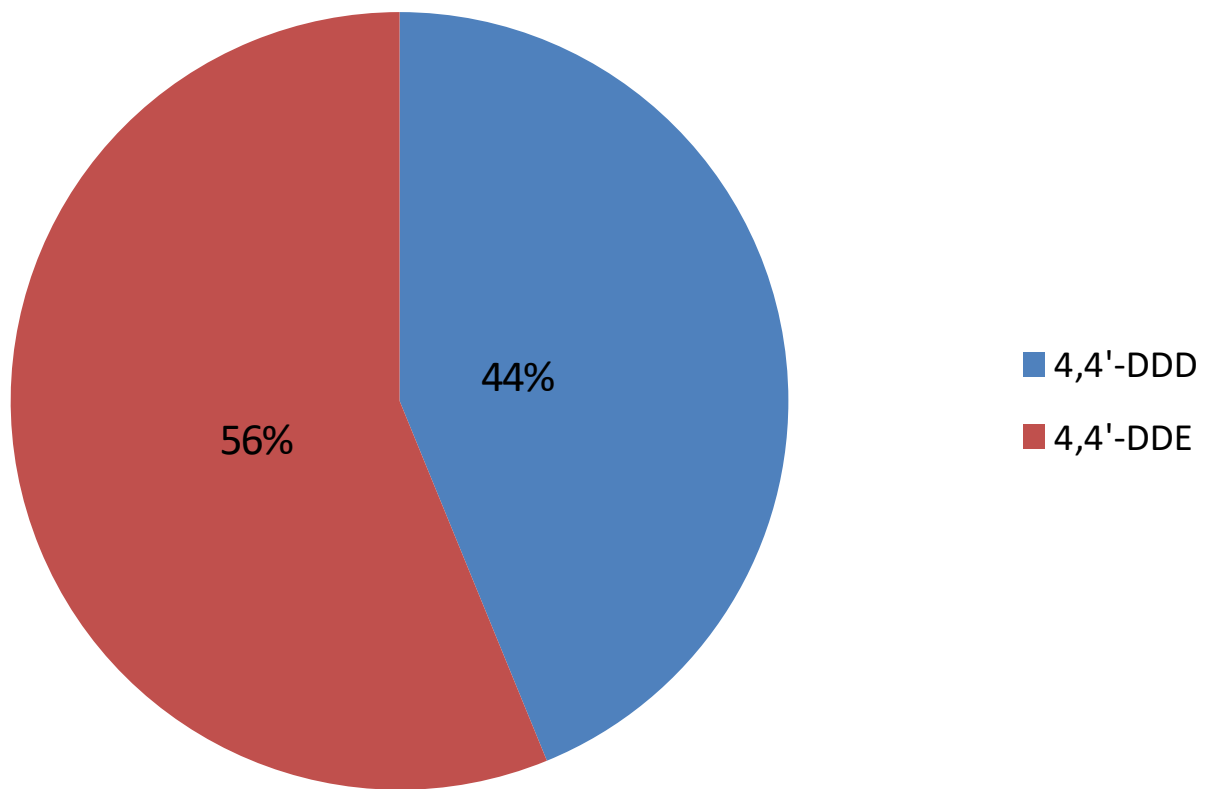
Figure 3: Total DDT concentrations (ng/g) in conch tissues. Only one site (BSS-7) was above MDL.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of DDT in Vieques ranged from below limits of detection to 0.194 ng/g, with only one sample (BSS-7) having detectable levels of DDT.

**Spatial Patterns:** Statistically, there are no differences (Dunn's test,  $\alpha=0.05$ ) between the strata.

**Comparison with Seafood Safety Guidelines:** When compared with conservative EPA values for subsistence fishing (16 meals per month), DDT concentrations in conch are 2 orders of magnitude below levels of concerns.





*Figure 4: Distribution of DDT associated analytes for the one sample that had detectable DDT. DDD and DDE are both breakdown products of the DDT parent material.*

Discussion: A previous study (Pait et al 2010) found elevated levels of DDT in sediments on the south shore of Vieques. DDT values in conch in this study were qualitatively lower than what was reported for queen conch in Florida (Glazer et al 2008). DDT was not detected in conch in St. Thomas (Apeti et al 2014), but that dataset was not statistically different from the Vieques data presented here (Wilcoxon test,  $\alpha=0.05$ ). Despite previous studies finding high concentrations of DDT on the south shore of Vieques, concentrations in conch were below detection limits for all but one sample. This might be explained by DDT uptake/sequestration rates in conch, or it may be because the previously observed DDT hotspots were quite localized to a lagoon near Playa Chiva and there is not widespread DDT contamination on the island. For the one sample that did have detectable DDT, the constituents of the DDT were limited to breakdown products (DDD and DDE, Figure 4), rather than the parent material (DDT). This suggests that this is not “new” DDT (i.e. from a leaking barrel or illegal uses), but is DDT that has been in the environment and slowly breaking down over time.



Figure 5: Aluminum concentrations ( $\mu\text{g/g}$ ) in conch tissues. All samples were above the MDL.

## Aluminum

Background: Aluminum (Al) is the most common metallic element in the Earth's crust.

Uses: Aluminum has a wide range of uses due to its malleability, lightweight nature and resistance to corrosion. Common uses include cans, foils, kitchen utensils, window frames, beer kegs, munitions and airplane parts. It is also used in alloys with copper, manganese, magnesium and silicon (RSC 2016a).

Environmental effects: Aluminum is generally not considered to be toxic in the marine environment, although toxicity to fish has been reported in acidified fresh waters (Baker and Schofield 1982).

Conch Tissue Concentrations in Vieques: Conch tissue concentrations of aluminum in Vieques ranged from 13.1  $\mu\text{g/g}$  to 61.2  $\mu\text{g/g}$ , with a mean of 33.7  $\mu\text{g/g}$ .

Spatial Patterns: Statistically, the Mosquito Pier stratum was higher than Bahia Salinas del Sur (Dunn's test,  $\alpha=0.05$ ,  $p=0.028$ ).

Discussion: The maximum observed aluminum values in queen conch in Vieques were lower than what was measured in St. Thomas (USVI, Apeti et al. 2014), but there were not statistically significant differences between these datasets (Wilcoxon test,  $\alpha=0.05$ ). The results of this study suggest that, despite the use of aluminum in military projectiles, there is no evidence that the history of military activities in Vieques has elevated the aluminum levels in conch, either when comparing the eastern side of the island (BSS and EH) to the western side (MP), or when comparing the data from Vieques to that of nearby St. Thomas (USVI).

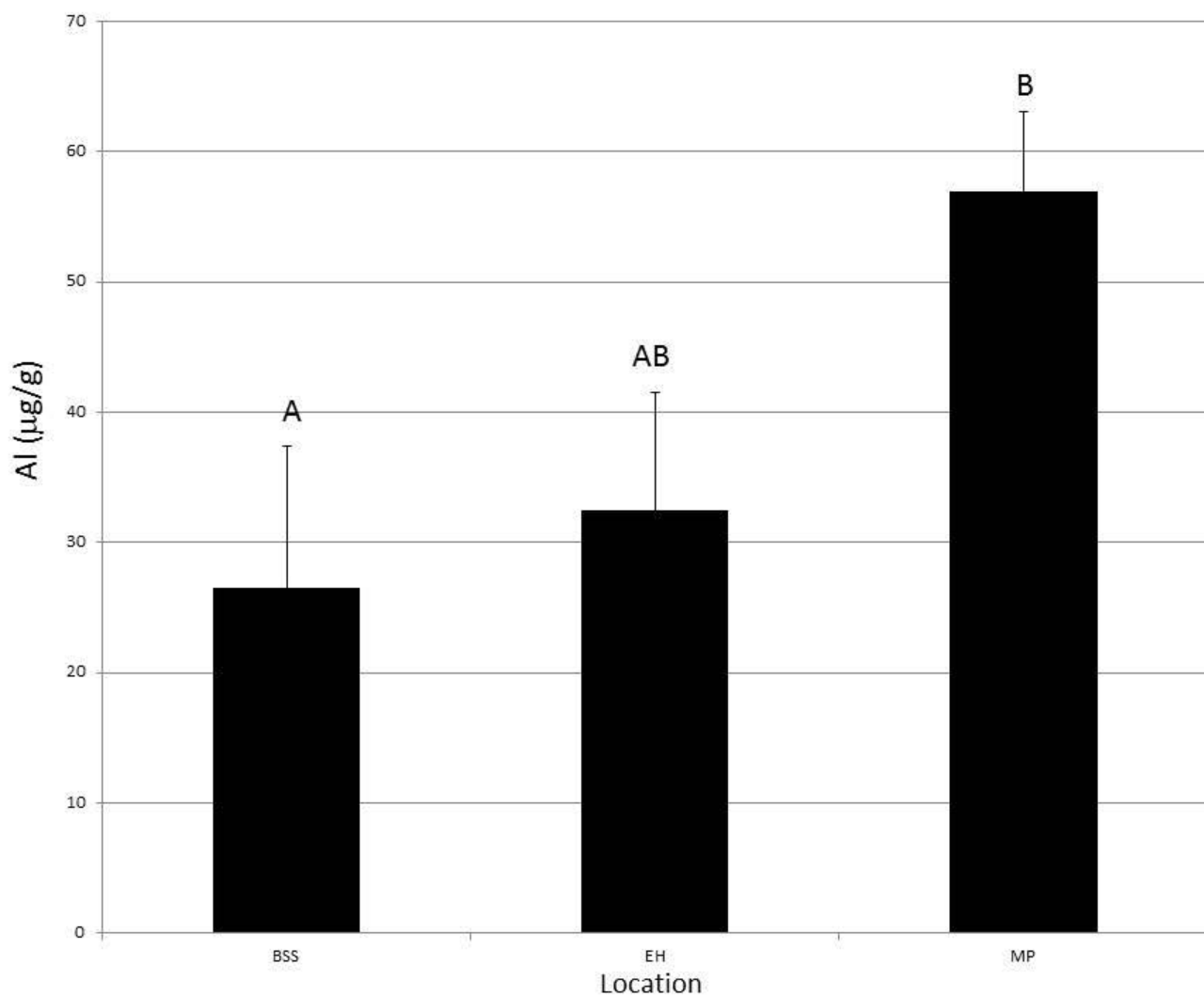


Figure 6: Aluminum (Al) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation. Letter groupings show statistically significant differences between strata (Dunn's test  $\alpha=0.05$ )

## Antimony

**Background:** Antimony (Sb) is a metalloid element that naturally occurs in the Earth's crust. Mining and use of antimony has increased the amount of antimony present in the environment.

**Uses:** Uses of antimony include as a component in semi-conductors, and a variety of alloys and compounds which are used for batteries, bullets, cable sheathing, flame retardants, and enamels (RSC 2016b).

**Environmental effects:** In the aquatic environment, antimony has been demonstrated to have both acute and chronic toxicity to both animals and plants, although there is very little data for marine systems (EPA 1980).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of antimony in Vieques ranged from 0.144 to 0.166  $\mu\text{g/g}$ , with a mean of 0.153  $\mu\text{g/g}$ . Because antimony is naturally occurring in the environment (i.e. unlikely to have a concentration of zero), samples with concentration below the MDL are reported as the MDL value. However, all of the samples had concentration that were below the detection limit, meaning there is substantial uncertainty in these data.



Figure 7: Antimony (Sb) concentrations ( $\mu\text{g/g}$ ). All values were below MDL.

**Spatial Patterns:** There are no statistically significant differences between the three sampling areas (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Antimony was not quantified in other published queen conch studies in the region, so no data is available for comparison. Although antimony is used in bullets (Ackermann et al. 2009), the low concentrations (below MDL) and lack of significant spatial differences between the three sampling areas does not suggest that historical military activities have impacted environmental levels of antimony.



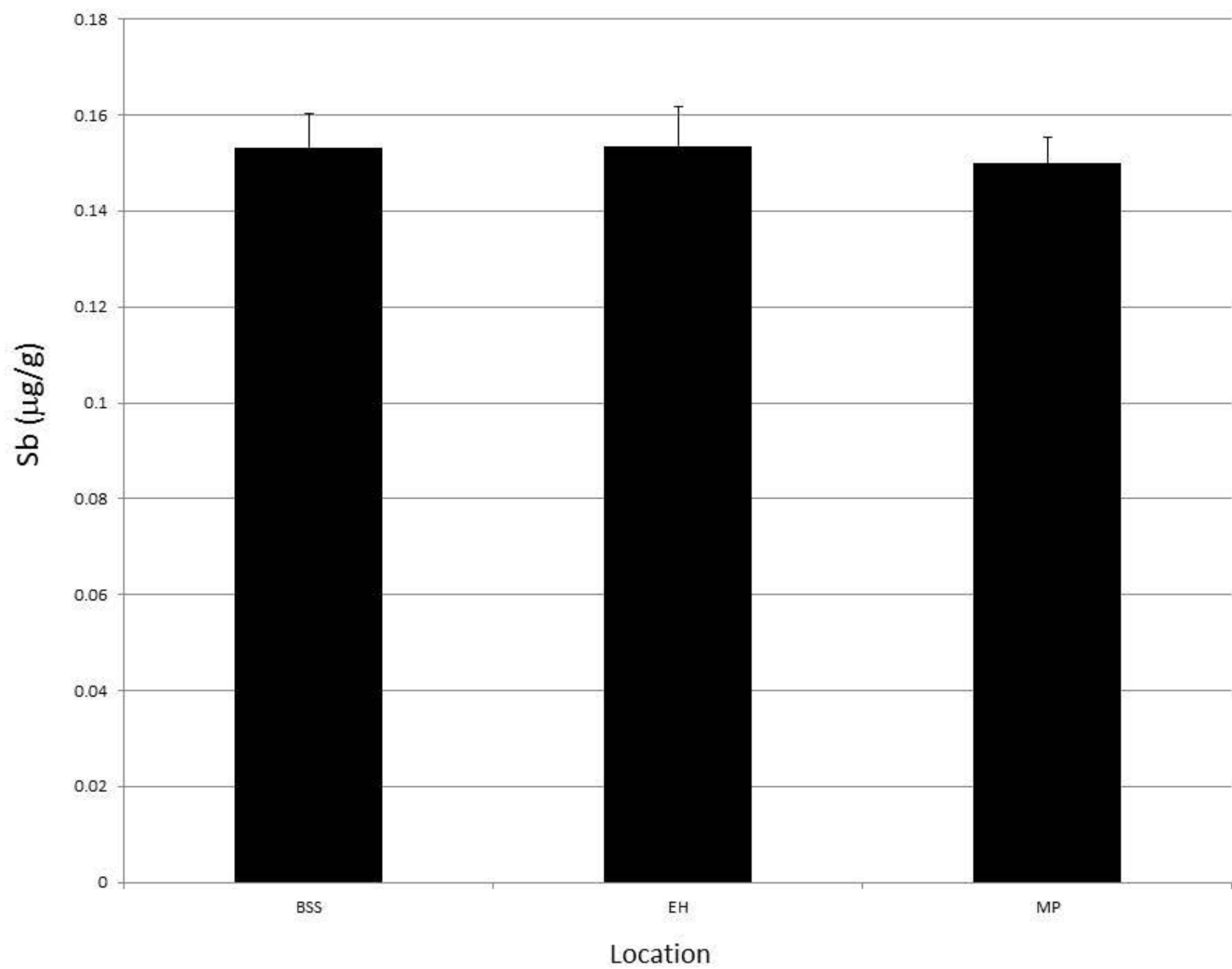


Figure 8: Antimony (Sb) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.

## Arsenic

**Background:** Arsenic (As) is a metalloid element that naturally occurs in the Earth's crust. It can exist as either an inorganic or organic compound. Mining and use of arsenic has increased the amount of arsenic present in the environment.

**Uses:** Arsenic has been widely used for centuries in applications ranging from pharmaceuticals to agriculture. Although arsenic use has declined in recently years due to concerns over toxicity, the most common uses of arsenic are pesticides, herbicides, desiccants, wood treatments and growth stimulants for agricultural crops and livestock (Eisler 1988). Arsenic can also be released into the environment through smelting. Inorganic forms of arsenic are generally much more toxic than organic forms.



Figure 9: Arsenic concentrations ( $\mu\text{g/g}$ ) in conch tissues. All concentrations were above the MDL.

**Environmental effects:** Arsenic is a known carcinogen, mutagen and teratogen. Its adverse effects have been quantified in humans, various mammalian species and fish, as well as in plants and invertebrates (Eisler 1988, Novellini et al. 2003). Marine species tend to accumulate more arsenic than freshwater species, although biomagnification does not occur. Chronic fish effects occur at tissue concentrations of  $2\text{--}5\text{ mg kg}^{-1}$  (McIntyre and Linton 2011).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of arsenic in Vieques ranged from  $4.18\text{ }\mu\text{g/g}$  to  $20.2\text{ }\mu\text{g/g}$ , with a mean of  $9.50\text{ }\mu\text{g/g}$ .

**Spatial Patterns:** There were no statistically significant (Dunn's test,  $\alpha=0.05$ ) differences between the strata.

**Comparison with Seafood Safety Guidelines:** When compared with conservative EPA values for subsistence fishing (16 meals per month, see Table 5), maximum observed inorganic arsenic concentrations in conch are above levels of concern.

**Discussion:** There were no statistically significant differences (Wilcoxon test,  $\alpha=0.05$ ) between the Vieques data presented here and data for arsenic in queen conch from St. Thomas (Apeti et al 2014), although the maximum observed values were slightly higher in Vieques (20  $\mu\text{g/g}$ ) than in St. Thomas (13  $\mu\text{g/g}$ , Table 6). Half of the samples measured in this study exceeded very conservative EPA seafood consumption guidelines for arsenic. However, this is not unique to Vieques as published values from Cuba, Florida and the Virgin Islands (Table 6) also exceed this guideline, which is based on 16 meals per month. Based on the maximum values measured in this study, the guidelines for four meals of conch per month would not be exceeded by Vieques concentrations. In addition to natural (crustal) sources, arsenic can enter the coastal environment from a variety of sources including treated wood, insecticides and herbicides. The lack of spatial differences between the three areas of the island, and between Vieques and near by St. Thomas do not suggest that former land uses (including military activities) had an effect on arsenic concentrations in the marine environment of Vieques.

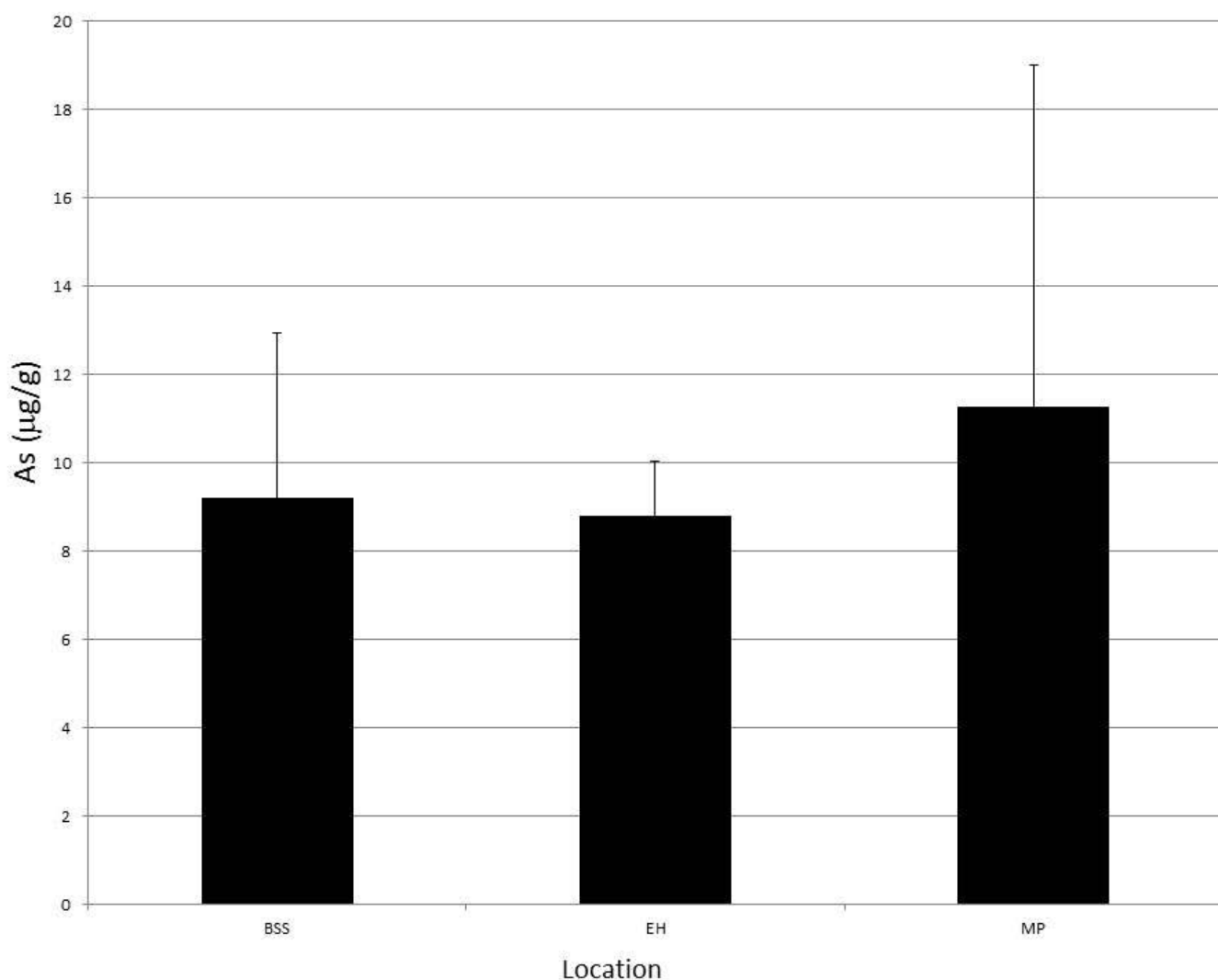


Figure 10: Arsenic (As) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.

## Barium

**Background:** Barium (Ba) soft, silvery metal that naturally occurs in the Earth's crust. Human uses of barium have the potential to increase the concentration of barium in the environment.

**Uses:** Compared to other metals, barium is not extensively used, but applications include in drilling fluids (gas/oil), paint, glassmaking and in x-ray radiography, as barium sulfate. Historically it was also used in rat poisons and in fireworks (RSC 2016d).

**Environmental effects:** All barium compounds are toxic, but because it readily forms insoluble salts (e.g. barium sulfate, barium carbonate), danger to aquatic biota is relatively low (Neff and Sauer, 1995).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of barium in conch in Vieques ranged from 0.036 to 0.285  $\mu\text{g/g}$ , with a mean of 0.18  $\mu\text{g/g}$ .



Figure 11: Barium (Ba) concentrations ( $\mu\text{g/g}$ ). All sites were above the MDL.

**Spatial Patterns:** There are no statistically significant differences between the three strata (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Barium was not quantified in queen conch in other studies in the region (Table 6), so no comparison is possible. There are no obvious potential sources of barium (large hospitals, oil/gas drilling) on Vieques and levels of barium likely represent background (natural) levels.

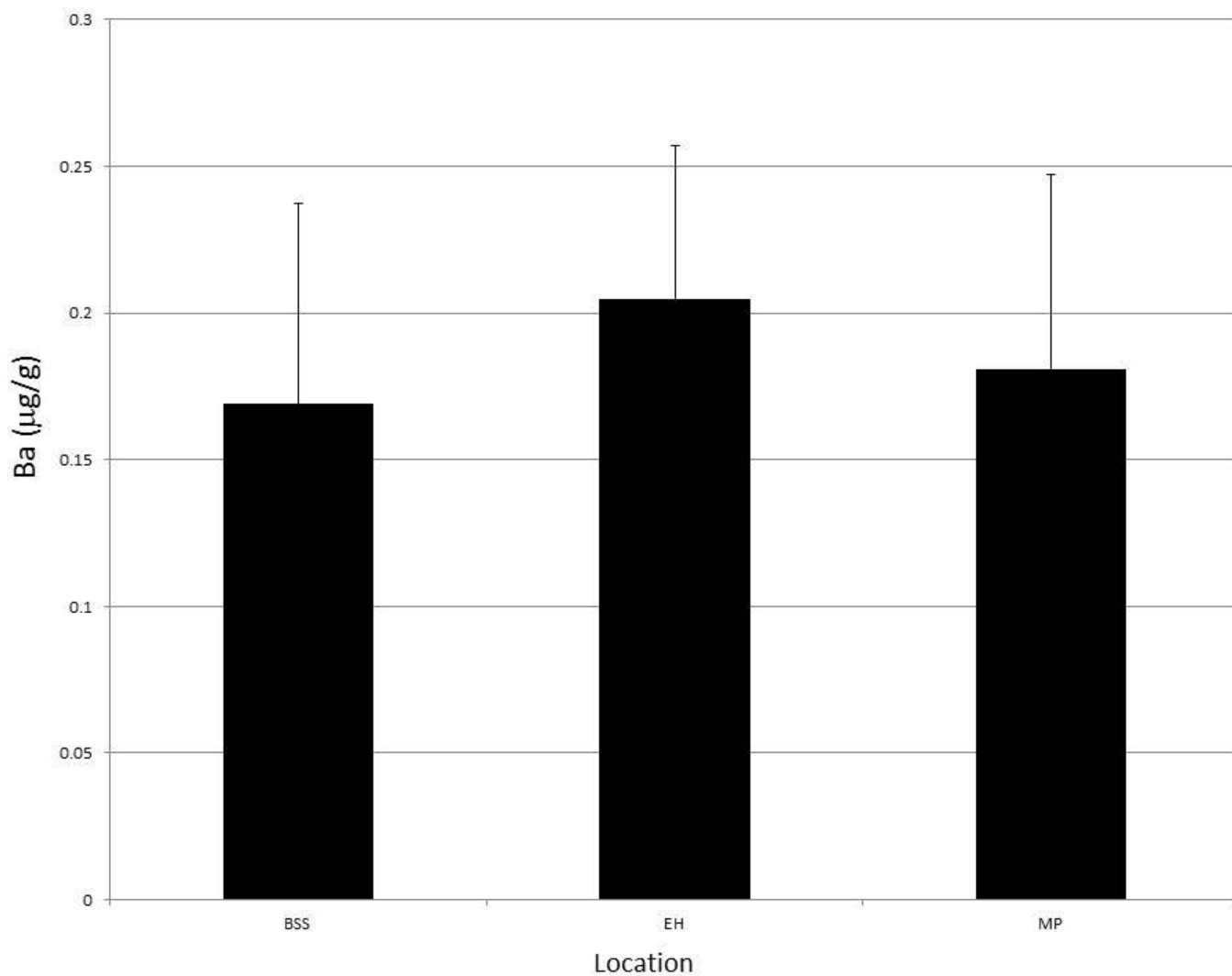


Figure 11: Barium (Ba) concentrations ( $\mu\text{g/g}$ ). All sites were above the MDL.



## Beryllium

**Background:** Beryllium (Be) is a soft, low density metal that occurs naturally in the Earth's crust. Mining and use of beryllium has increased the amount of beryllium present in the environment.

**Uses:** Uses of beryllium include as structural material in aircraft, missiles and spacecraft, and in alloys with nickel or copper to make springs, electrodes, and non-sparking tools (RSC 2016d). Beryllium can also enter the environment through the mining and use of coal (Irwin et al. 1997).



Figure 13: Beryllium (Be) concentrations ( $\mu\text{g/g}$ ). All samples were below the MDL.

**Environmental effects:** Beryllium is both toxic and carcinogenic to humans as well as other mammals. Teratogenic effects have been documented for snails and salamanders, and acute toxicity observed for freshwater fish (Irwin et al. 1997). Relatively little information exists on beryllium in the marine environment.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of beryllium in Vieques ranged from 0.008 to 0.009  $\mu\text{g/g}$ , with a mean of 0.0086  $\mu\text{g/g}$ . All samples were below the MDL, but because beryllium is naturally occurring in the environment (i.e. unlikely to be zero), samples with concentration below the MDL are reported as the MDL value.

**Spatial Patterns:** There are no statistically significant differences between the three sampling areas (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Beryllium was not quantified in queen conch in other studies in the region, so no comparison is possible. Levels of measured beryllium were below the method detection limit. This, in combination with the lack of a spatial pattern between the sampling areas, suggests that beryllium in conch is not elevated due to previous military activities.

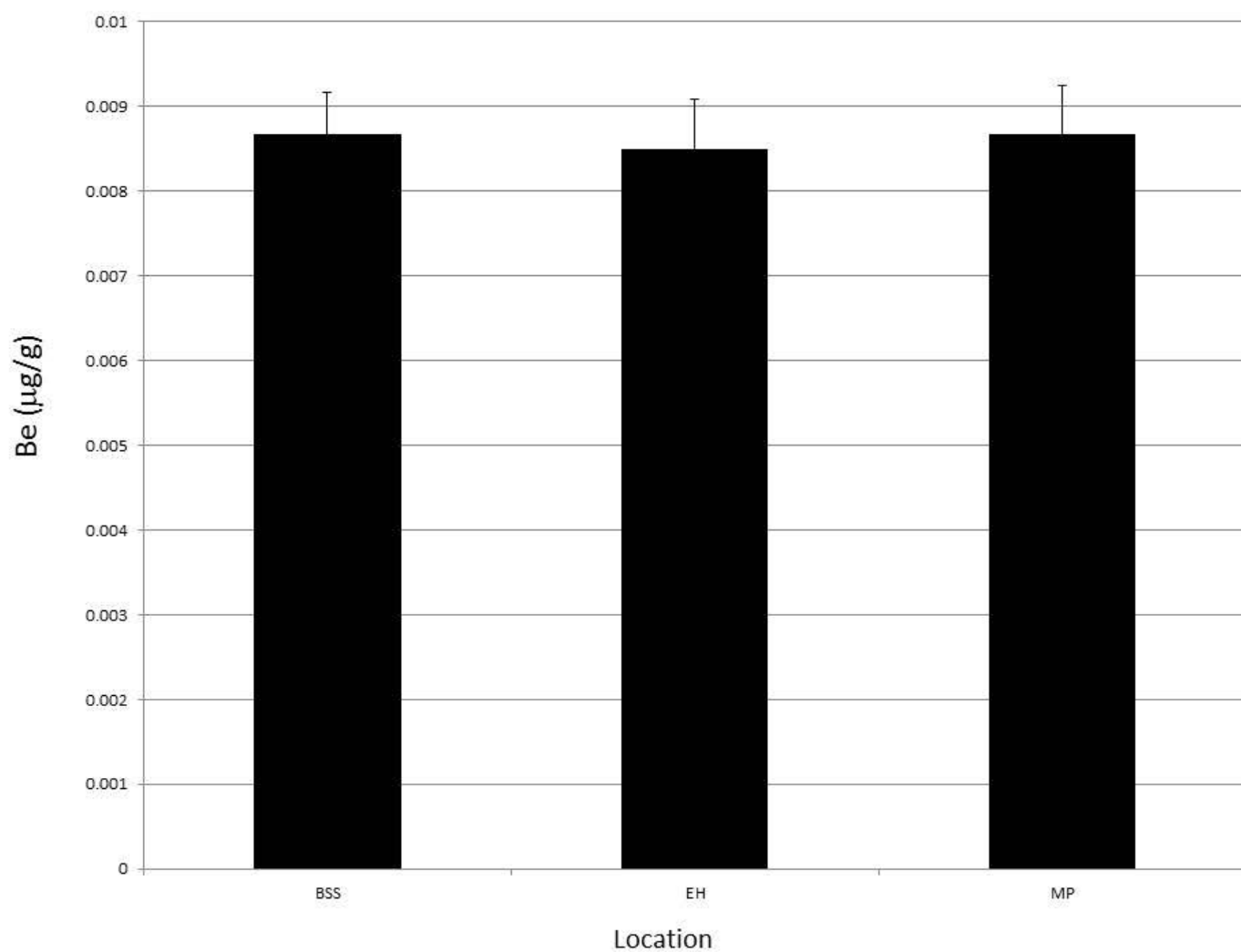


Figure 14: Beryllium (Be) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Cadmium

**Background:** Cadmium (Cd) is a metallic element that naturally occurs in the Earth's crust. Mining and use of cadmium has increased the amount of cadmium present in the environment.

**Uses:** Cadmium has historically been widely used in batteries, pigments and in electroplating. Cadmium use is being reduced due to concerns over toxicity (RSC 2016e).

**Environmental effects:** Although cadmium is a minor nutrient for plant growth, it is relatively toxic to aquatic organisms. Toxicity to sea urchins (Edullantes and Galapate, 2014, Dermeche et al. 2012), bivalves, crustaceans, conch tissue invertebrates and fish has been reported (EPA 2001), including effects on development and reproduction in several invertebrate species, and the potential to impede osmoregulation in herring larvae (USDHHS 1999; Eisler 1985). Cadmium inhibits fertilization in scleractinian coral at relatively high concentrations (5,000 g/L, Reichelt-Brushett and Harrison, 2005).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of cadmium in Vieques ranged from 0.097 to 0.688 µg/g, with a mean of 0.35 µg/g.

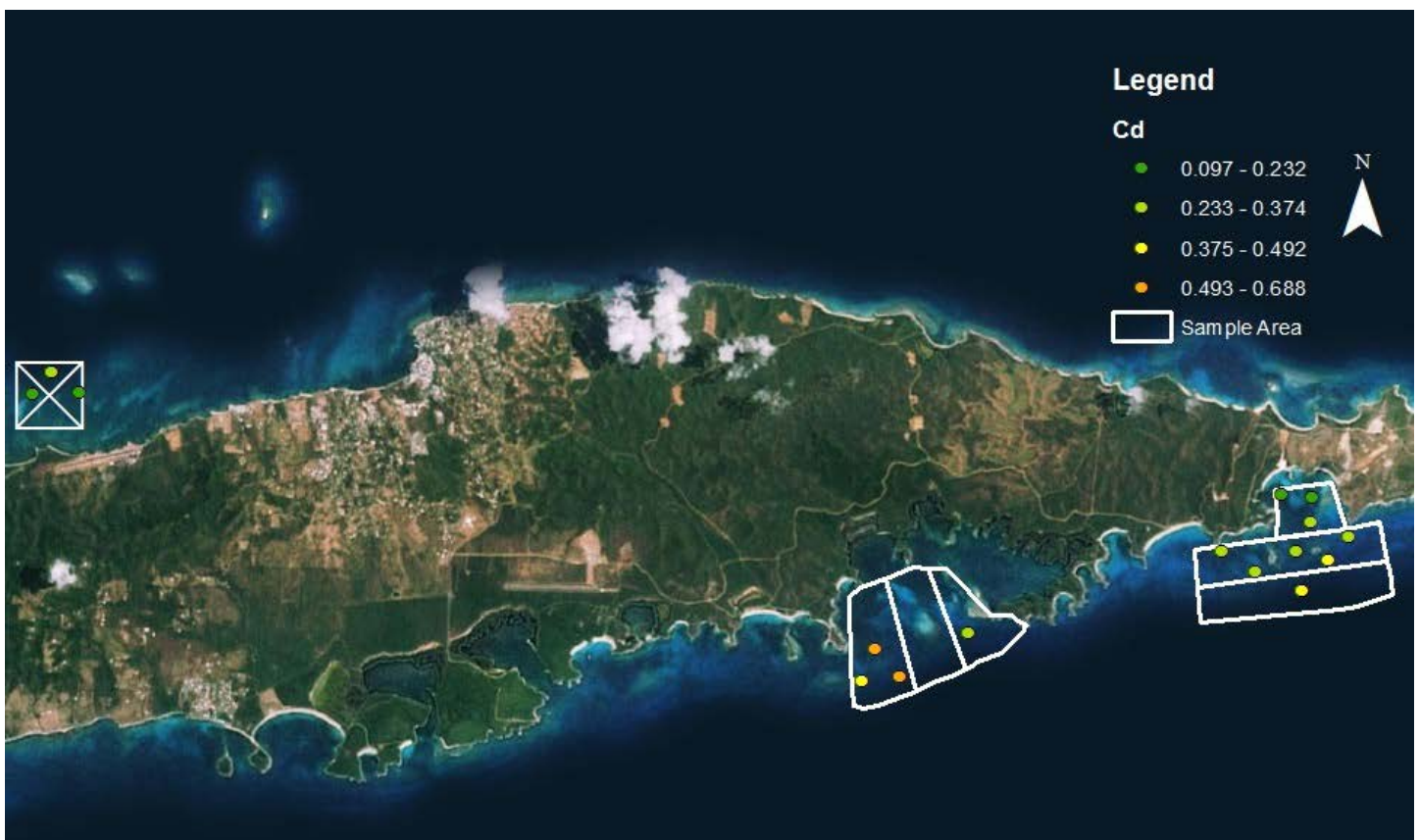


Figure 15: Cadmium (Cd) concentrations (µg/g). All samples were above the MDL.

**Spatial Patterns:** The Ensenada Honda (EH) sampling area on the southeast side of the island was statistically higher (Dunn's test,  $\alpha=0.05$ ,  $p=0.0173$ ) than the Mosquito Pier (MP) sampling area on the northwest side of the island.

**Comparison with Seafood Safety Guidelines:** When compared with conservative EPA values for subsistence fishing (16 eight ounce meals per month, see Table 6), maximum observed cadmium concentrations in conch are above levels of concern.



Discussion: Cadmium values reported here for queen conch in Vieques are lower than what has been reported elsewhere in the region, although there were no statistically significant differences (Wilcoxon test,  $\alpha=0.05$ ) with St. Thomas (Apeti et al., 2014). Although one of the eastern sampling areas (EH) is higher than the western comparison area (MP, Figure 17), because these values are not elevated compared to other studies in the region, it does not appear that prior land uses, including military activities, have resulted in Cd in conch in Vieques that is unusually high for the region. All but two of the samples measured in this study exceeded very conservative EPA seafood consumption guidelines for cadmium. However, this is not unique to Vieques, as published values from Cuba, Florida and the Virgin Islands (Table 6) also exceed this guideline, which is based on 16 meals per month. Based on the maximum values measured in this study, the guidelines for four meals of conch per month would not be exceeded by concentrations reported for Vieques in this study.

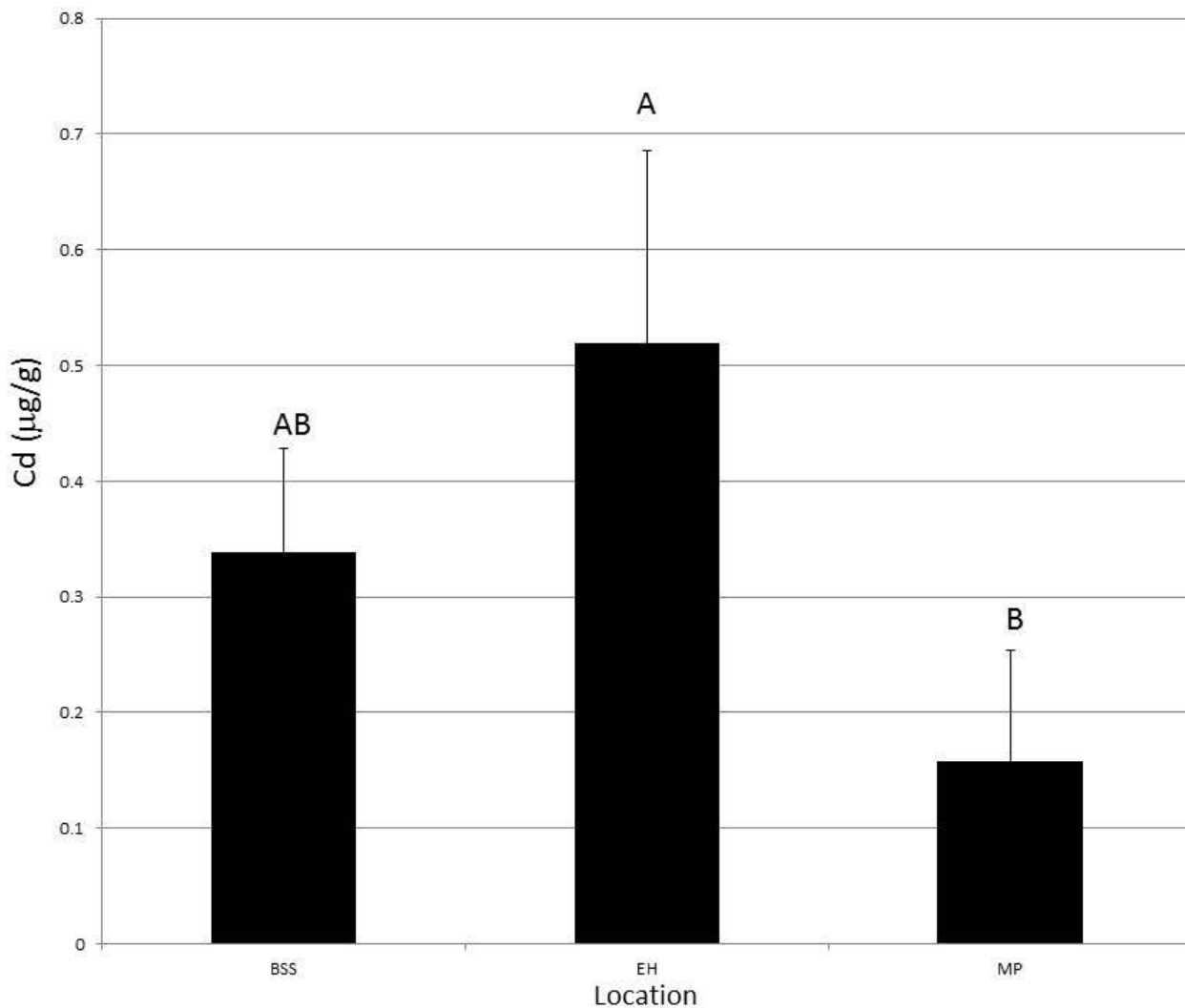


Figure 16: Cadmium (Cd) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation. Letter groupings show statistically significant differences between strata (Dunn's test  $p=0.05$ )

## Chromium

**Background:** Chromium (Cr) is a metallic element that naturally occurs in the Earth's crust. Mining and use of chromium has increased the amount of this metal present in the environment.

**Uses:** Chromium has a variety of uses including leather tanning, stainless steel, metallic plating and in industrial catalysts (RSC 2016f). It is an essential nutrient for plants and animals but can be toxic in excessive concentrations.

**Environmental effects:** Chromium has been shown to reduce survival and fecundity in the cladoceran *Daphnia magna*, decreased reproductive success in the sea urchin *Paracentrotus lividus* (Novellini et al. 2003) and reduced growth in fingerling chinook salmon (*Oncorhynchus tshawytscha*) (Eisler 1986).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of chromium in Vieques ranged from 0.95  $\mu\text{g/g}$  to 2.08  $\mu\text{g/g}$ , with a mean of 1.45  $\mu\text{g/g}$ .

**Spatial Patterns:** There are no statistically significant differences between the strata in the Bay (Dunn's test,  $\alpha=0.05$ ).



Figure 17: Chromium (Cr) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Discussion:** Concentrations of chromium in queen conch in Vieques were statistically higher than those observed in St. Thomas (Apeti et al., 2014, Table 6, Wilcoxon test,  $\alpha=0.05$ ). Unfortunately, chromium was not quantified in other queen conch studies in the region, so a broader comparison is not possible. However, based on the lack of spatial differences between the sampling areas, there is no clear evidence that former land uses are affecting chromium concentrations in queen conch. Additional sampling, both in Vieques and across the region could better quantify if and to what extent chromium is elevated in conch in Vieques.

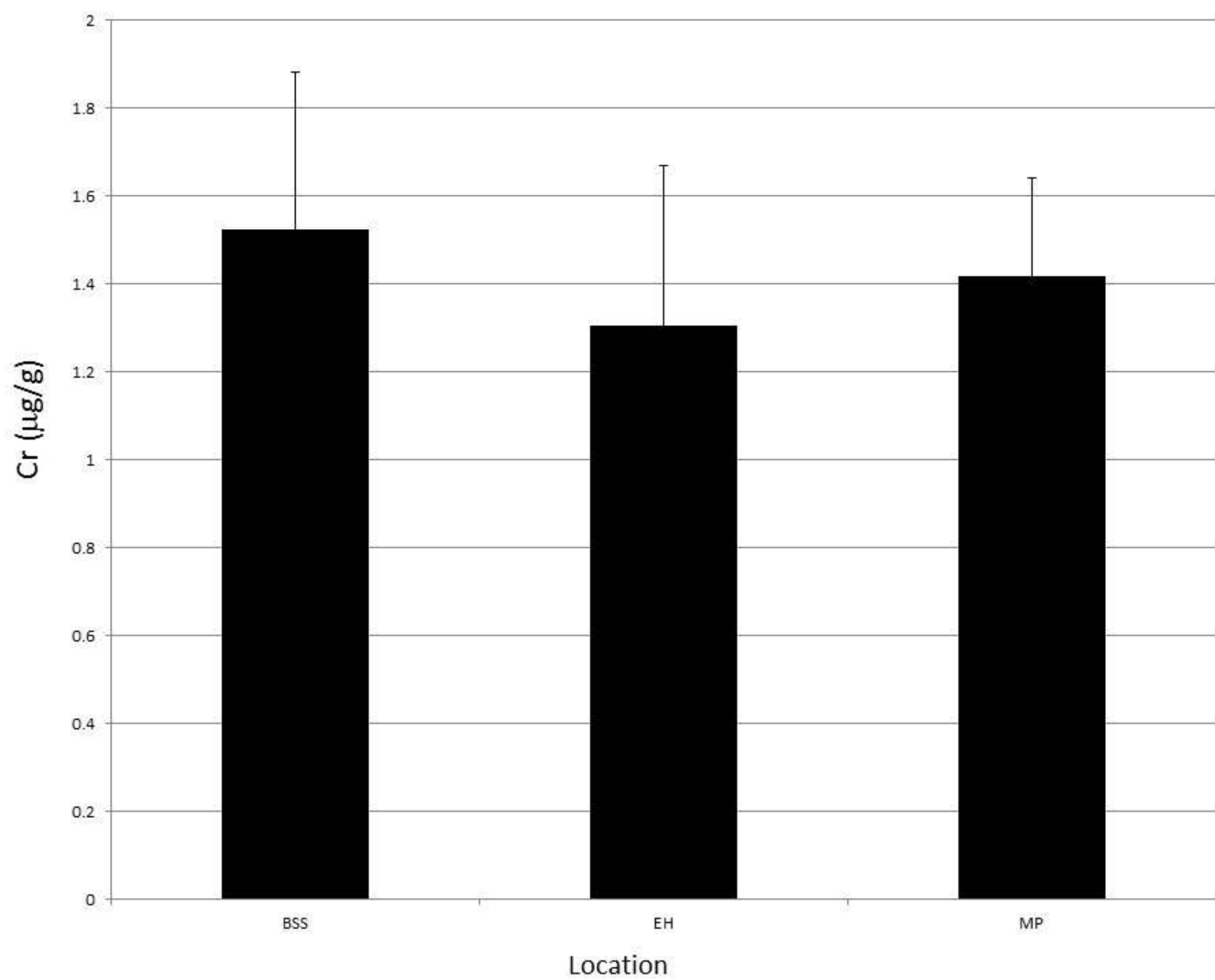


Figure 18: Chromium (Cr) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.

## Cobalt

**Background:** Cobalt (Co) is a metallic element with magnetic properties that naturally occurs in the Earth's crust. Mining and use of cobalt has increased the amount of cobalt present in the environment.

**Uses:** Cobalt is used in magnets, and in alloys in jet and gas turbine engines, electroplating and as a coloring agent in paint, pottery and enamels (RSC 2016g).

**Environmental effects:** Cobalt is an essential trace element as part of vitamin B12; however, large doses of cobalt can be toxic to humans and animals. High ambient concentrations of cobalt cause acute toxicity in a variety of marine organisms (diatoms, copepods, nematodes, fish, lobster, crab, shrimp) with larval stages often being more sensitive to elevated cobalt than adult organisms (Nagpal 2004).



Figure 19: Cobalt (Co) concentrations ( $\mu\text{g/g}$ ). All samples were below the MDL.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of cobalt in Vieques were below the MDL and ranged from 0.30 to 0.045  $\mu\text{g/g}$ , with a mean of 0.033  $\mu\text{g/g}$ . Because cobalt is naturally occurring in the environment (i.e. unlikely to have a concentration of zero), samples with concentration below the MDL are reported as the MDL value.

**Spatial Patterns:** There were no statistically significant differences between strata for cobalt in queen conch tissue (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Cobalt was not quantified in queen conch in other studies in the region (Table 6) preventing a comparison of data. Because all samples had concentrations below the MDL, it is unlikely that cobalt in conch in Vieques is high for the region.

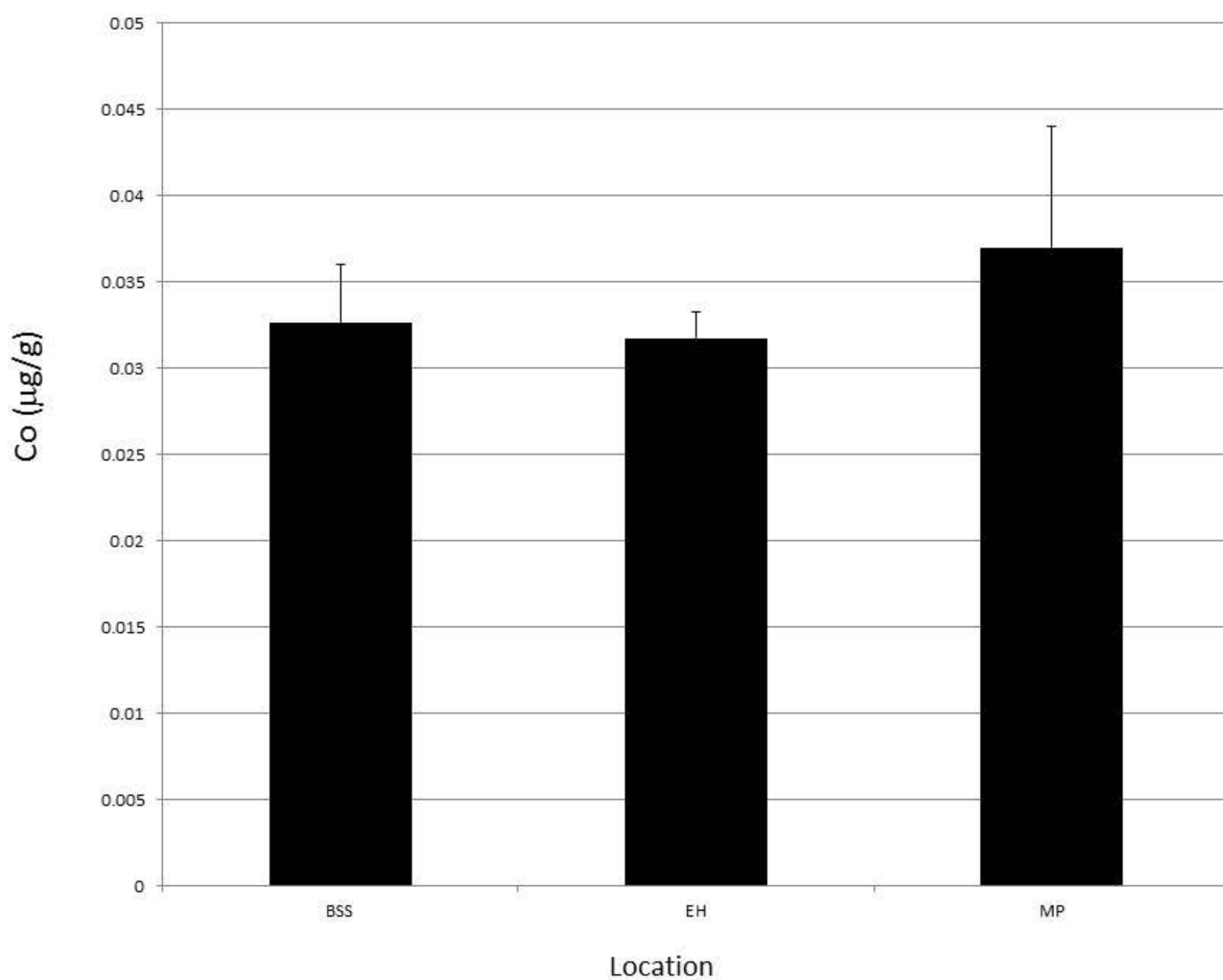


Figure 20: Cobalt (Co) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.



## Copper

**Background:** Copper (Cu) is a metallic element with excellent conductivity that naturally occurs in the Earth's crust. Mining and use of copper has increased the amount of copper present in the environment.

**Uses:** Copper has a wide array of uses ranging from coins to wires to pipes to pesticides to industrial materials (e.g. heat exchangers) to anti-fouling paints to alloys. Copper is an essential micronutrient for plants and animals but can have adverse effects at high concentrations.



Figure 21: Copper (Cu) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Environmental effects:** In aquatic environments, copper can have deleterious effects on reproduction and development in mysid shrimp (Eisler 1998), and sea urchins (Edullantes and Galpate, 2014; Dermèche et al. 2012; Novellini et al. 2003). In corals, copper concentrations of  $20 \mu\text{g/L}$  have been shown to significantly reduce fertilization success in brain coral *Goniastrea aspera* (Reichelt-Brushett and Harrison, 2005). At copper concentrations at or above  $75 \mu\text{g/L}$ , fertilization success was reduced to one percent or less. Fertilization success was also significantly reduced in the coral *Acropora longicyathus* at  $24 \mu\text{g/L}$ , a similar concentration level at which effects were observed in *G. aspera*.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of copper in Vieques ranged from  $4.77 \mu\text{g/g}$  to  $26.3 \mu\text{g/g}$ , with a mean of  $11.25 \mu\text{g/g}$ .

**Spatial Patterns:** There were not statistically significant differences between the three sampling areas (Dunn's test). Qualitatively, Ensenada Honda appeared to be slightly lower than Mosquito Pier or Bahía Salinas del Sur.

Discussion: Copper concentrations in queen conch were qualitatively similar to what was observed in Cuba, but lower, by an order of magnitude than values from Florida (Table 6). Statistically, copper in conch in Vieques was lower (Wilcoxon test,  $\alpha=0.05$ ) than what was measured in St. Thomas (Apeti et al 2014; Table 6). Based on these regional and local patterns in copper in queen conch, it does not appear that historical land use is driving spatial patterns of copper in conch in the marine waters of Vieques.

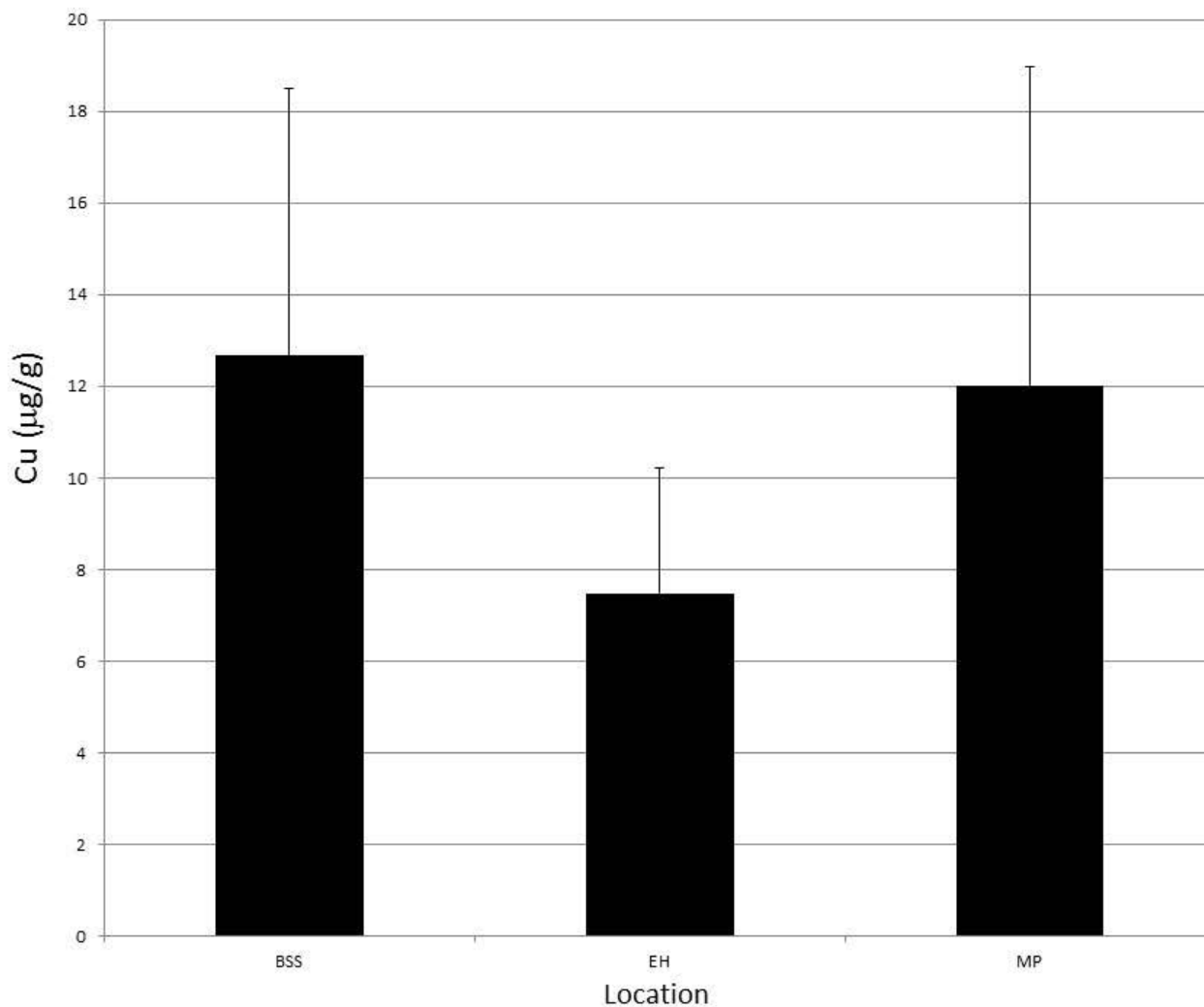


Figure 22: Copper (Cu) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Iron

**Background:** Iron (Fe) is a metallic element that by mass is the most abundant element in the Earth's crust. Mining and use of iron has increased the amount of iron present in the environment.

**Uses:** Iron is used in many materials for construction and manufacturing including steel, stainless steel and cast iron. Iron is an essential nutrient for both plants and animals.

**Environmental effects:** Iron is generally not considered to be toxic in the environment, but like aluminum it can provide some context about the source of other crustal elements (e.g. erosion versus pollution) (RSC 2016f).



Figure 23: Iron (Fe) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of iron in Vieques ranged from 60  $\mu\text{g/g}$  to 197  $\mu\text{g/g}$ , with a mean of 128  $\mu\text{g/g}$ .

**Spatial Patterns:** Statistically, Mosquito Pier had higher concentration of iron in queen conch than Bahia Salinas del Sur (Dunn's test,  $\alpha=0.05$ ,  $p=0.0316$ ).

**Discussion:** Qualitatively, iron in queen conch is lower in Vieques than what was measured in St. Thomas (Apeti et al 2014; Table 6), although this was not statistically significant (Wilcoxon test,  $\alpha=0.05$ ). Even though iron can be a major component of munitions casings and the bombing range targets (e.g. vehicles), spatial patterns, both regionally and among the three sampling areas of this study, do not suggest that military activities have resulted in elevated levels of iron in queen conch.



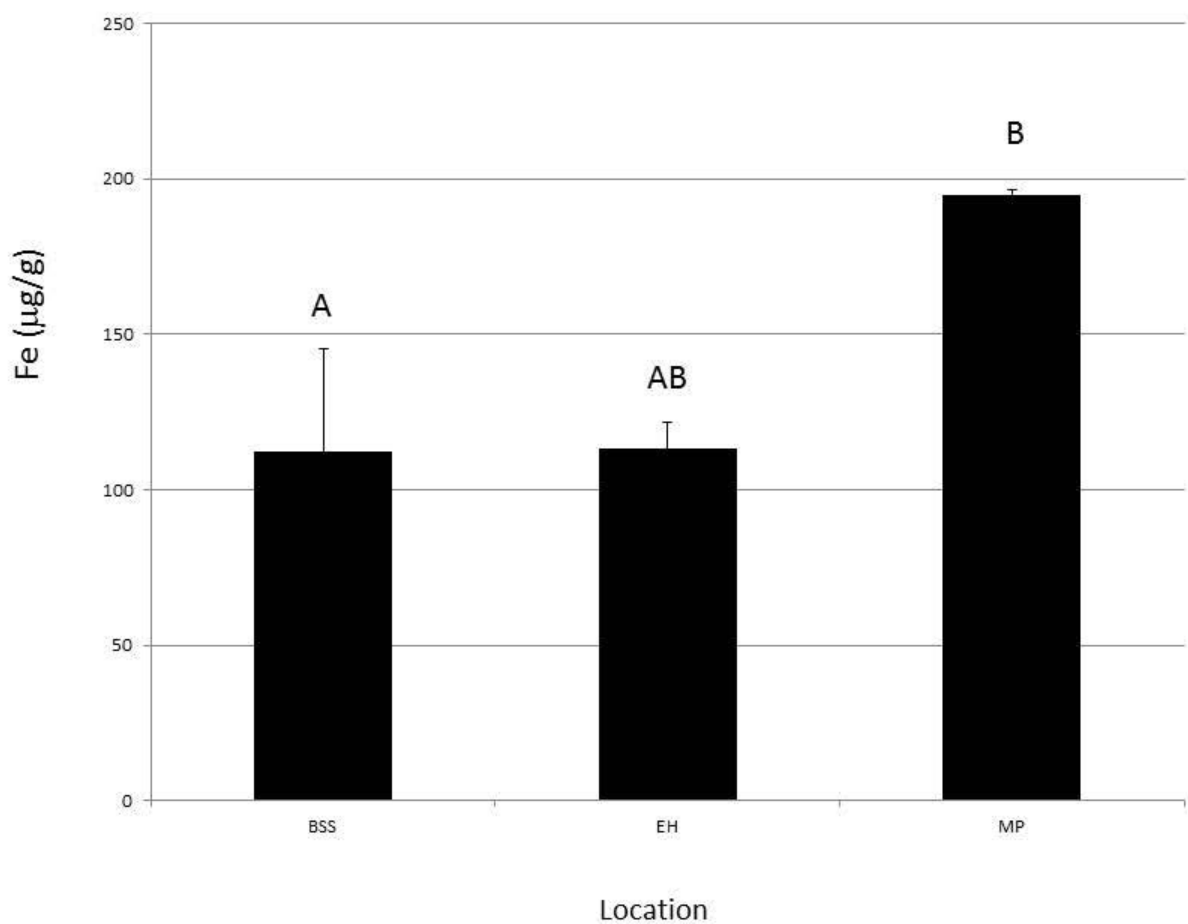


Figure 24: Iron (Fe) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation. Letter groupings show statistically significant differences between strata (Dunn's test  $\alpha=0.05$ )

## Lead

**Background:** Lead (Pb) is a malleable, corrosion resistant metallic element that naturally occurs in the Earth's crust. Mining and use of lead has increased the amount of lead present in the environment.

**Uses:** Lead has been widely used for centuries in pipes, pewter, paints, pottery glazes, insecticides, hair dyes and gasoline additives. These uses have been greatly reduced due to concerns over lead toxicity. Lead is still widely used in car batteries, ammunition, weights (e.g. barbells and dive belts), crystal glass, solder and radiation protection (RSC 2016i).

**Environmental effects:** Lead has no known nutritional role in plant or animal health. It can be acutely toxic as well as a carcinogen and teratogen (RSC 2016i). Reproductive effects on sea urchins have been previously documented (Novellini et al. 2003, Dermeche et al. 2012).



Figure 25: Lead (Pb) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of lead in Vieques ranged from 0.024 to 0.072  $\mu\text{g/g}$ , with a mean of 0.053  $\mu\text{g/g}$ .

**Spatial Patterns:** There were no statistically significant differences between the three sample areas for lead in conch (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Lead concentrations in queen conch of Vieques were qualitatively lower than what was reported for Cuba, and significantly lower (Wilcoxon test,  $\alpha=0.05$ ) than St. Thomas (Table 6). Based on the regional comparison and the lack of spatial differences within this study, it does not appear that historical land uses, including military activities, have impacted the levels of lead in queen conch tissues.

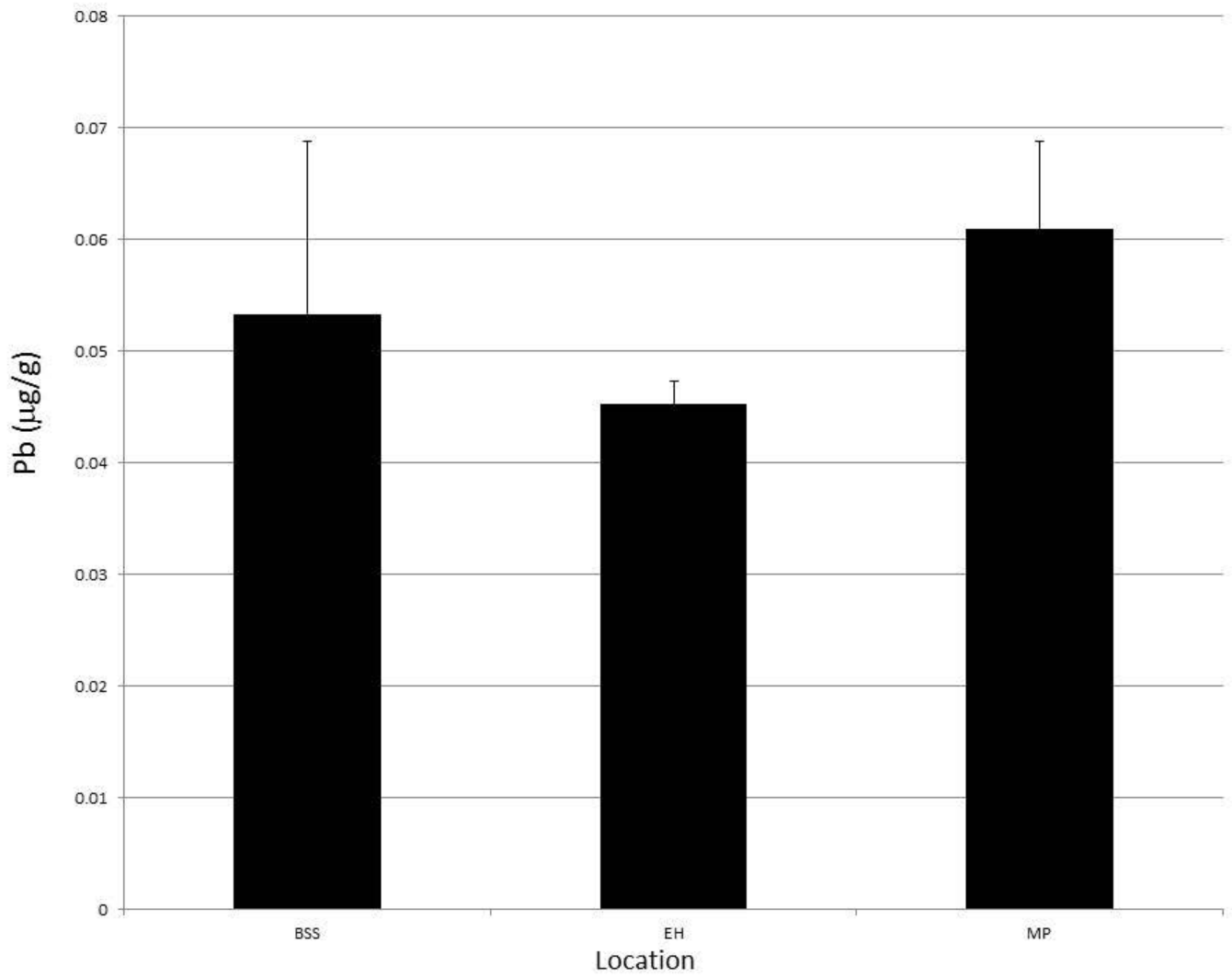


Figure 26: Lead (Pb) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Lithium

**Background:** Lithium (Li) is a soft silvery metal. It has the lowest density of any metal and reacts very exothermically when exposed to water.

**Uses:** The primary use of lithium is in rechargeable batteries for such applications as mobile phones, laptop computer and electric vehicles. It is also used in some non-rechargeable batteries for pacemakers and clocks (RSC 2016j).



Figure 27: Lithium (Li) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Environmental effects:** Lithium has no known biological role and is toxic except in very small doses (RSC 2016j). In aquatic environments, lithium has been shown to be toxic to fish and invertebrates (Kszos et al. 2003).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of lead in Vieques ranged from 0.067  $\mu\text{g/g}$  to 0.118  $\mu\text{g/g}$ , with a mean of 0.09  $\mu\text{g/g}$ .

**Spatial Patterns:** There are no statistical differences between the three samples areas for lithium in conch tissues (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** Lithium was not quantified in queen conch in other studies in the region, so no comparison is possible. The lack of a spatial patterns between the sampling areas suggests that lithium in conch is not elevated due to previous military activities, but additional sampling across the region could better quantify the relatively magnitude of Li in conch in Vieques.

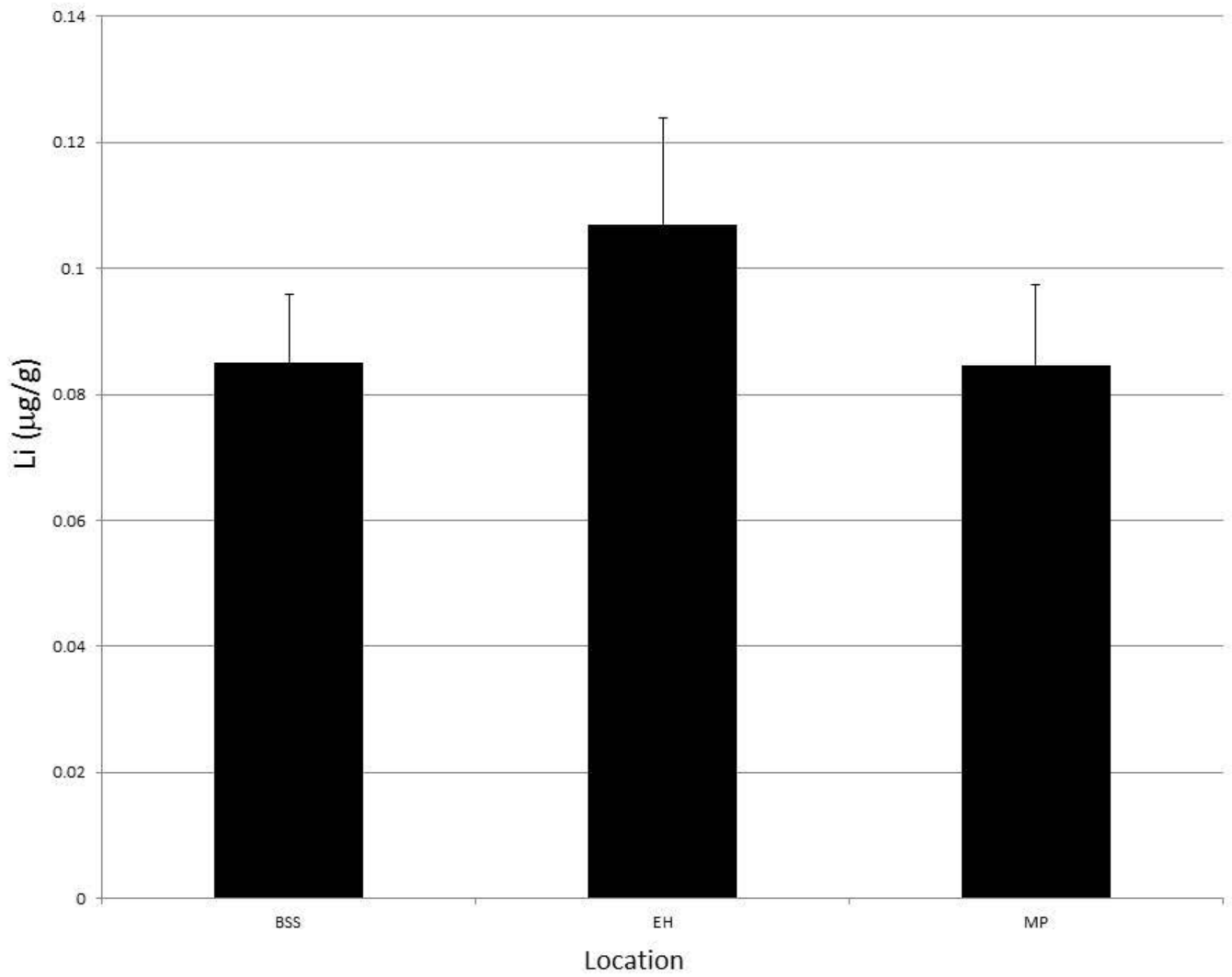


Figure 28: Lithium (Li) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.



## Manganese

**Background:** Manganese (Mn) is a brittle metallic element that naturally occurs in the Earth's crust. Mining and use of manganese has increased the amount of manganese present in the environment.

**Uses:** Because of its brittle nature, manganese is primarily used in alloys with steel and aluminum, as well as a catalyst, rubber additive, in fertilizers and in pesticides (RSC 2016k).



Figure 29: Manganese (Mn) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Environmental effects:** Manganese is an essential element for plants and animals, although it can be toxic to aquatic invertebrates at chronic high doses (Norwood et al. 2007). Studies have demonstrated that manganese, like other major and trace elements, does accumulate in corals (Whitall et al. 2014) and is primarily sequestered in the tissues, rather than the skeleton (Metian et al. 2014).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of manganese in Vieques ranged from 9.3  $\mu\text{g/g}$  to 63.9  $\mu\text{g/g}$ , with a mean of 33.9  $\mu\text{g/g}$ .

**Spatial Patterns:** There are no statistically significant differences between the three sample areas for manganese in conch (Dunn's test,  $\alpha=0.05$ ).

**Discussion:** There were no statistically significant differences (Wilcoxon test,  $\alpha=0.05$ ) between the Vieques data presented here and data for queen conch from St. Thomas (Apeti et al 2014), although concentrations in St. Thomas were, qualitatively, slightly higher (Table 6).

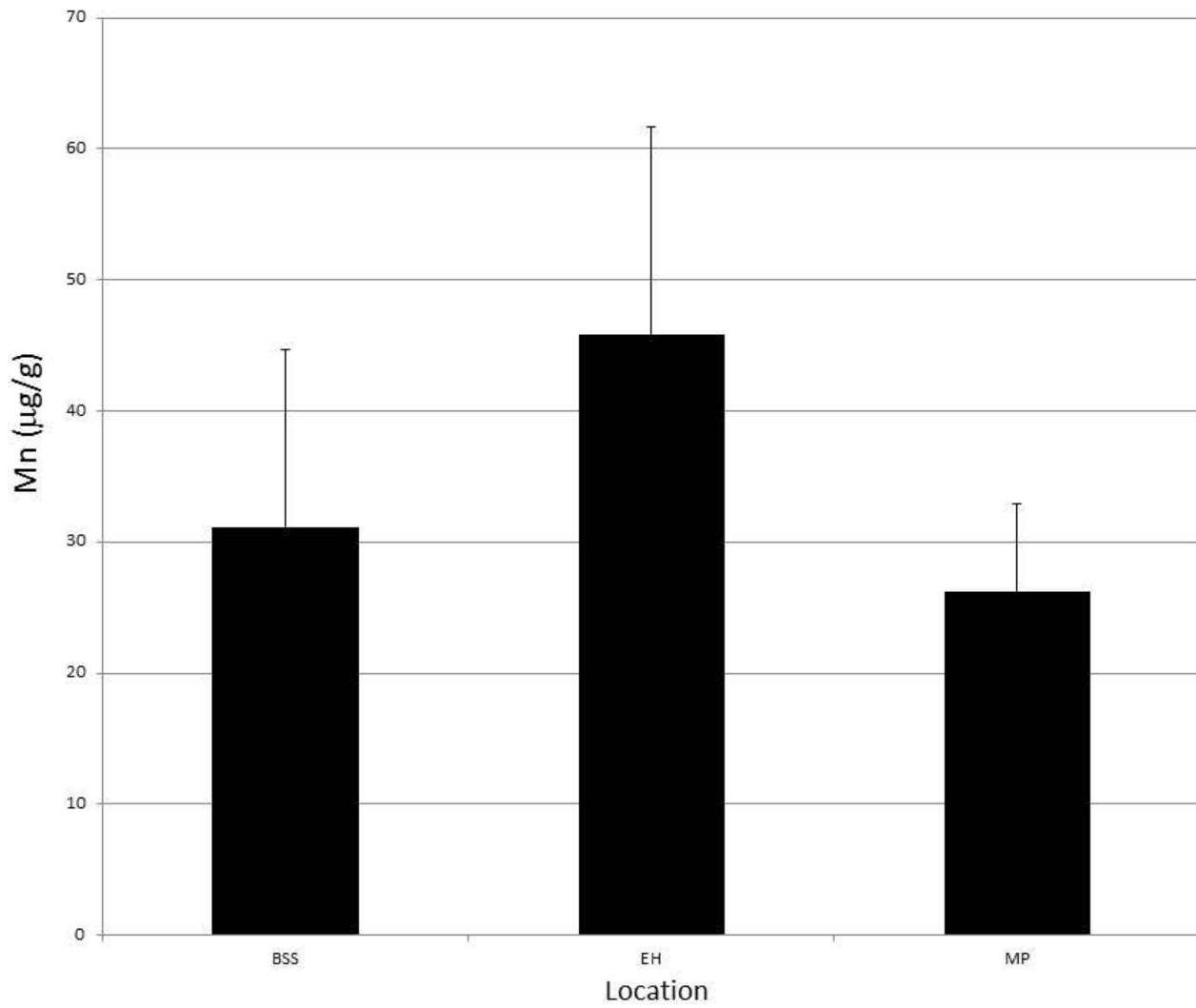


Figure 30: Manganese (Mn) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Mercury

**Background:** Mercury (Hg) is a naturally occurring heavy metal that is liquid at room temperature in its elemental form. It exists in natural geologic formations as a solid in various compounds. Mining and use of mercury has increased the amount of mercury present in the environment.

**Uses:** Historically, mercury was used in manufacturing, batteries, fluorescent lights, dental fillings, felt production and thermometers, but these uses have been gradually phased out due to toxicity concerns. It is currently used in the chemical industry as a catalyst, and in some electrical switches.

**Environmental effects:** Methyl mercury ( $\text{CH}_3\text{Hg}$ ) is the most toxic form of mercury. Mercury can be toxic to birds and invertebrates, and bioaccumulates in fish, which can have human health implications for fisheries species (USGS 2000). Mercury has been shown to be more toxic to sea urchins than other metals (Novellini et al. 2003). Although toxic effects of mercury on corals are not well understood, mercury uptake by corals has been previously demonstrated (e.g. Whitall et al. 2014; Guzman and Garcia, 2002), and mercury accumulates more in coral tissues than in the skeleton (Bastidas and Garcia 2004).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of mercury in Vieques ranged from 0.017  $\mu\text{g/g}$  to 0.045  $\mu\text{g/g}$ , with a mean of 0.028  $\mu\text{g/g}$ .

**Spatial Patterns:** There were no statistically significant differences between sampling areas for mercury in queen conch (Dunn's test,  $\alpha=0.05$ ).



Figure 31: Mercury (Hg) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Comparison with Seafood Safety Guidelines:** When compared with conservative EPA values for subsistence fishing (16 eight ounce meals per month, see Table 5), maximum observed mercury concentrations in conch are below levels of concern.

Discussion: There were no statistically significant differences (Wilcoxon test,  $\alpha=0.05$ ) between the Vieques data presented here and data for queen conch from St. Thomas (Apeti et al 2014); qualitatively, concentrations in St. Thomas are slightly higher. Concentrations from Florida were close to zero (Table 6). Based on the lack of regional and local (within island) spatial patterns, it is unlikely that former land use has impacted the levels of mercury in queen conch in Vieques.

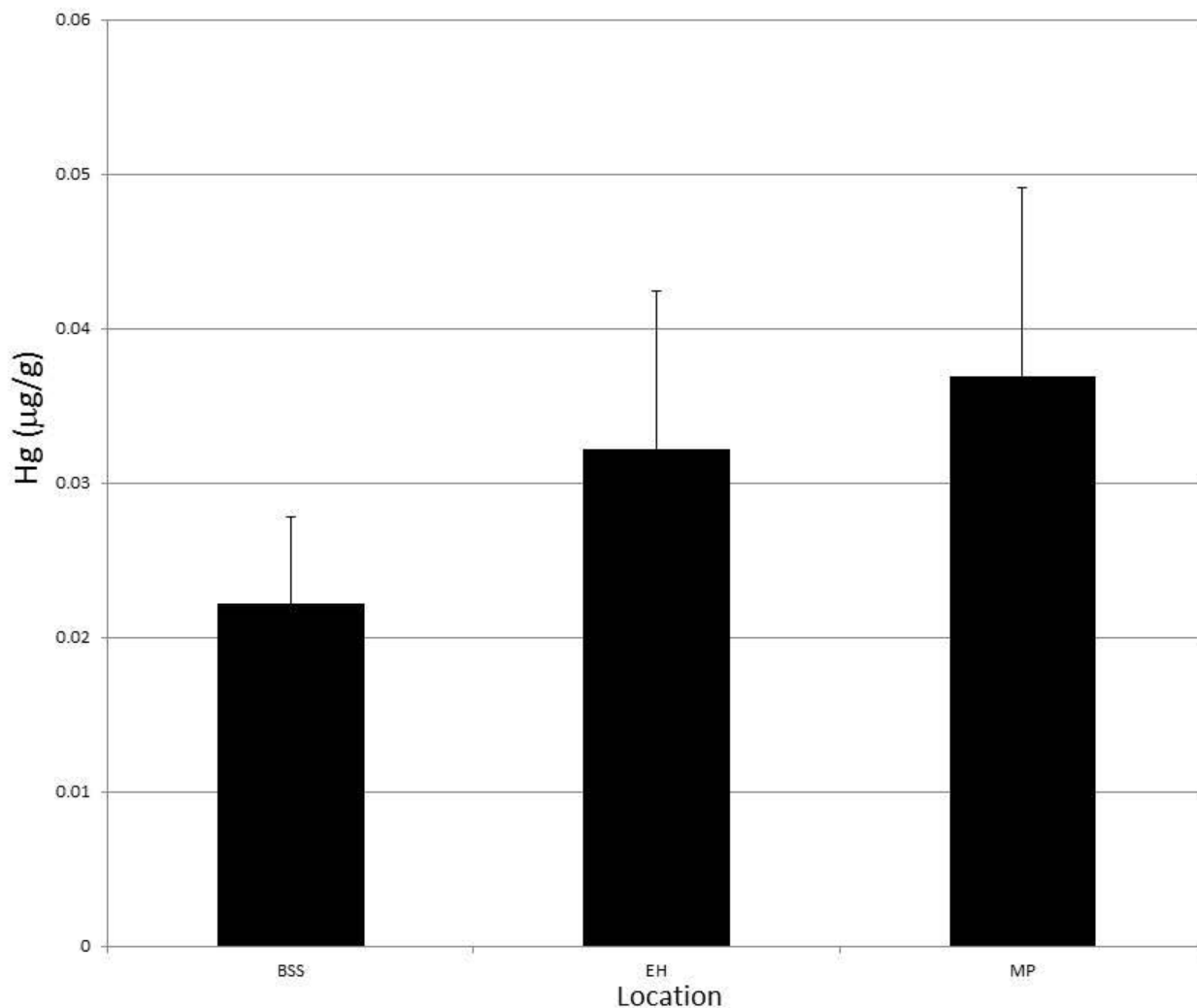


Figure 31: Mercury (Hg) concentrations (µg/g). All samples were above the MDL.



## Nickel

**Background:** Nickel (Ni) is a metallic element that naturally occurs in the Earth's crust. Mining and use of nickel has increased the amount of nickel present in the environment.

**Uses:** Nickel is used in batteries, coins, metal plating and a variety of alloys (e.g. stainless steel).

**Environmental effects:** Nickel has been shown to have adverse effects on sea urchins (Novellini et al. 2003), crustaceans and fish (Hunt 2002). Previous studies (e.g. Whitall et al. 2014) have shown that nickel accumulates in corals, and that water column concentrations of 9 mg/L cause mortality in *Pocillopora damicornis* larvae (Goh 1991).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of nickel in Vieques ranged from 1.13 to 3.81  $\mu\text{g/g}$ , with a mean of 2.11  $\mu\text{g/g}$ .

**Spatial Patterns:** Qualitatively, concentrations of nickel in conch on the southeastern side of the island appear higher than those at Mosquito Pier. However, these differences are not statistically significant (Dunn's test,  $\alpha=0.05$ ).



Figure 33: Nickel (Ni) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Discussion:** Statistically, nickel concentrations in conch in this study were significantly higher than observed in St. Thomas (Wilcoxon test,  $\alpha=0.05$ ) but an order of magnitude lower than measured in Florida (Table 6). This regional pattern, in combination with the lack of spatial differences within this study, suggests that historical land use, including military activities, have not resulted in unusually high nickel concentration in conch in Vieques.



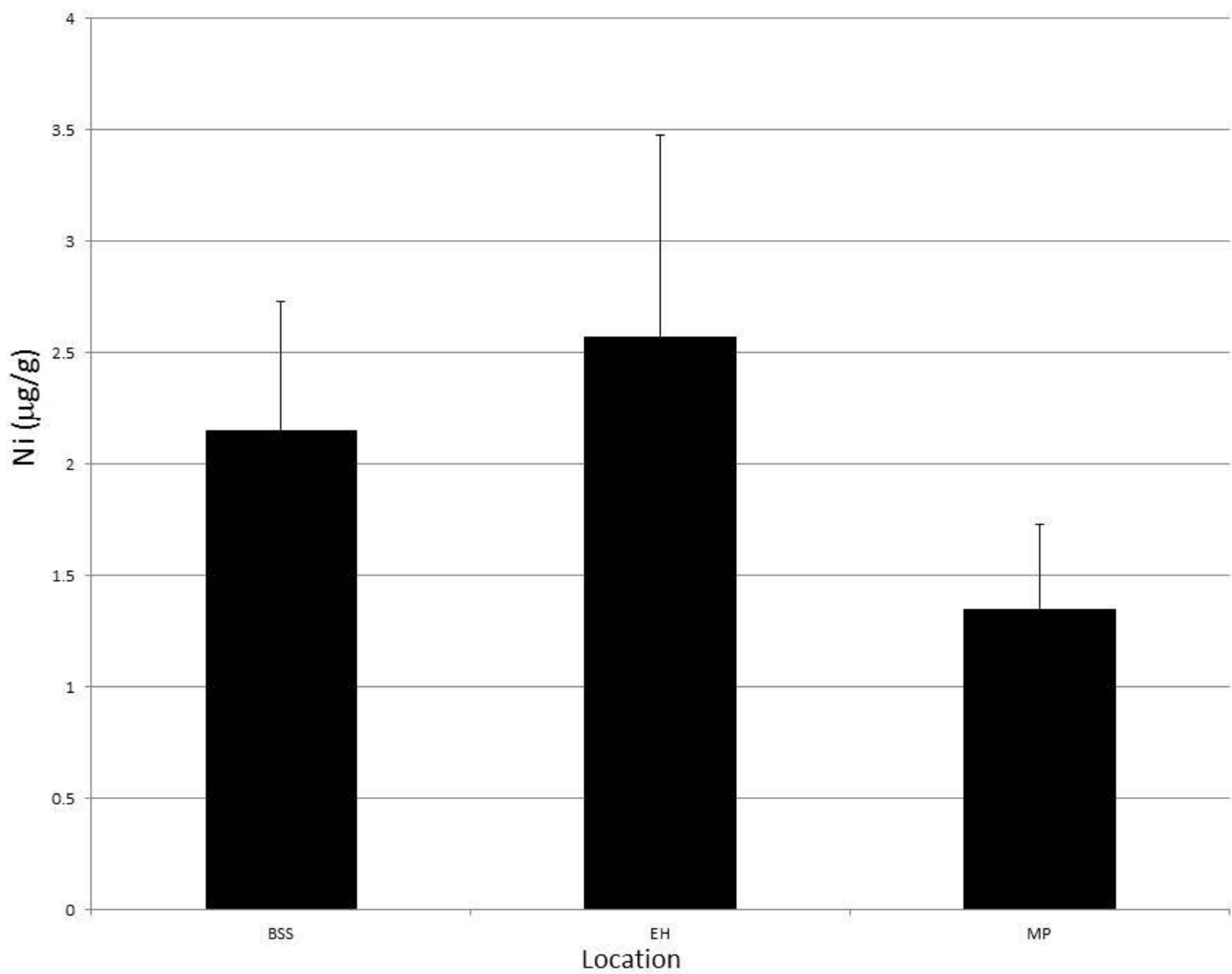


Figure 34: Nickel (Ni) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Selenium

**Background:** Selenium (Se) is a trace element (semi-metal) that naturally occurs in the Earth's crust. Mining and use of selenium has increased the amount of selenium present in the environment.

**Uses:** Selenium has a range of uses including as an additive in glass production, as a fungicide and in photocells, solar cells, photocopiers and rectifiers (RCS 2014i).

**Environmental effects:** Selenium is a micronutrient for some organisms including humans. Selenium can bioaccumulate and has been shown to be toxic to both invertebrates and fish at elevated concentrations (EPA 2014). Selenium's effect on coral reef ecosystems has not been well documented, but other studies have demonstrated that selenium does accumulate in corals (Whitall et al. 2014).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of selenium in Vieques ranged from 0.492  $\mu\text{g/g}$  to 0.967  $\mu\text{g/g}$ , with a mean of 0.652  $\mu\text{g/g}$ .

**Spatial Patterns:** There are no statistically significant differences between sampling areas for selenium in conch (Dunn's test,  $\alpha=0.05$ ).



Figure 35: Selenium (Se) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Comparison with Seafood Safety Guidelines:** When compared with conservative EPA values for subsistence fishing (16 eight ounce meals per month, see Table 5), maximum observed selenium concentrations in conch are not exceeded by concentrations measured in Vieques.

**Discussion:** Statistically, selenium concentrations in conch in this study were significantly higher than observed in St. Thomas (Wilcoxon test,  $\alpha=0.05$ ). However, the lack of spatial differences within this study suggests that historical land use, including military activities, have not resulted in unusually high selenium concentration in conch in Vieques.

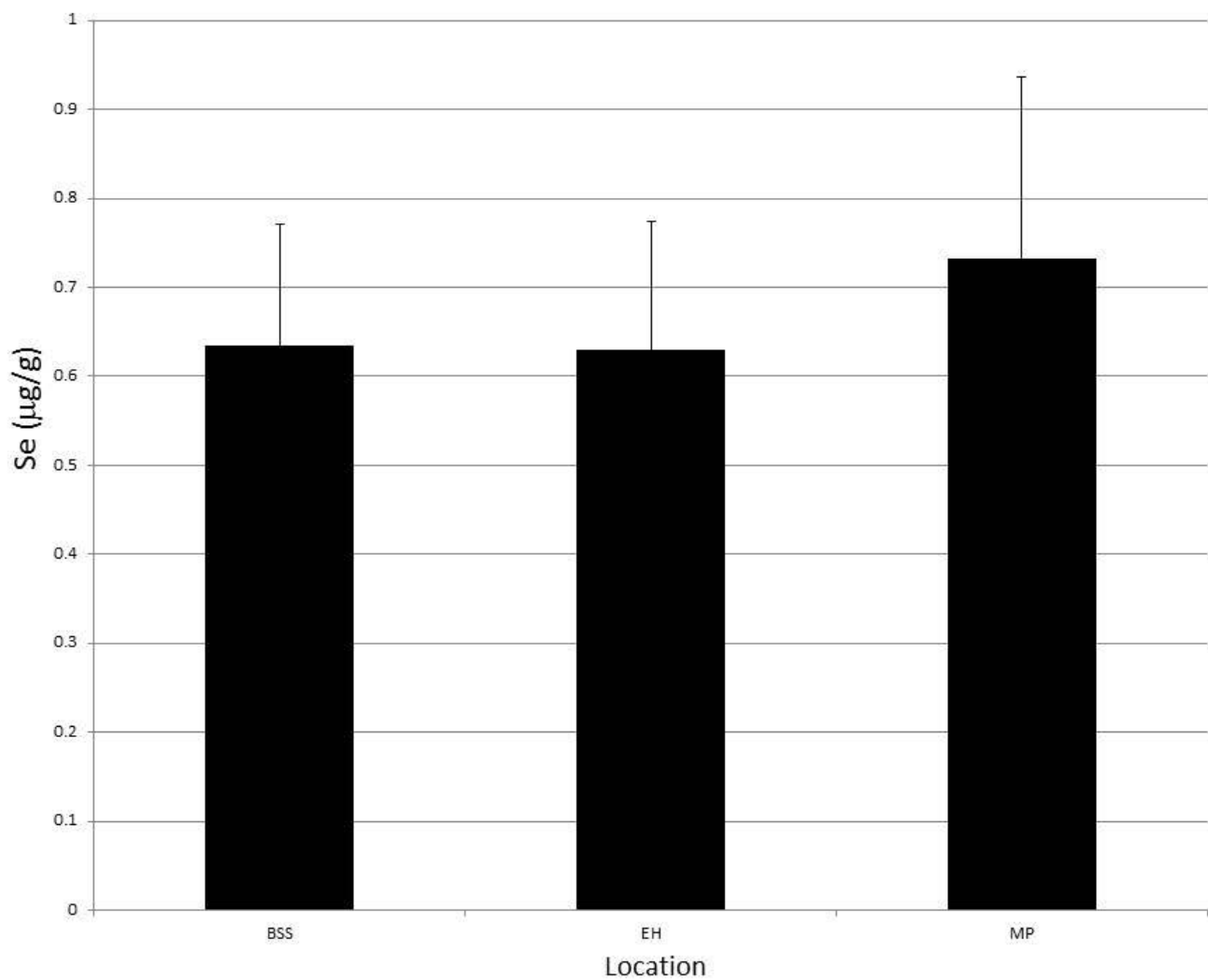


Figure 36: Selenium (Se) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Silver

**Background:** Silver (Ag) is a metallic element that naturally occurs in the Earth's crust. Mining and use of silver has increased the amount of silver present in the environment.

**Uses:** Silver is widely used including in jewelry, dental alloys, solder and brazing alloys, electrical contacts, batteries, circuits, photography and nanoparticles (RSC 2016b).

**Environmental effects:** Silver is one of the more toxic elements to plants and animals in the marine environment (Bryan 1984) including toxicity to bivalves, fish and phytoplankton.

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of silver in Vieques ranged from 0.043 µg/g to 0.206 µg/g, with a mean of 0.109 µg/g.

**Spatial Patterns:** Although EH is qualitatively higher than the other two strata, there were no statistically significant differences between strata for silver in queen conch (Dunn's test,  $\alpha=0.05$ ).



Figure 37: Silver (Ag) concentrations (µg/g). All samples were above the MDL.

**Discussion:** Qualitatively, silver concentrations in queen conch in this study are lower than observed in Florida and St. Thomas (Table 6); however, there were no statistically significant differences (Wilcoxon test,  $\alpha=0.05$ ) between the Vieques data presented here and data for queen conch from St. Thomas (Apeti et al 2014). This regional pattern, in combination with the lack of spatial differences within this study, suggests that historical land use, including military activities, have not resulted in unusually high silver concentrations in conch in Vieques.

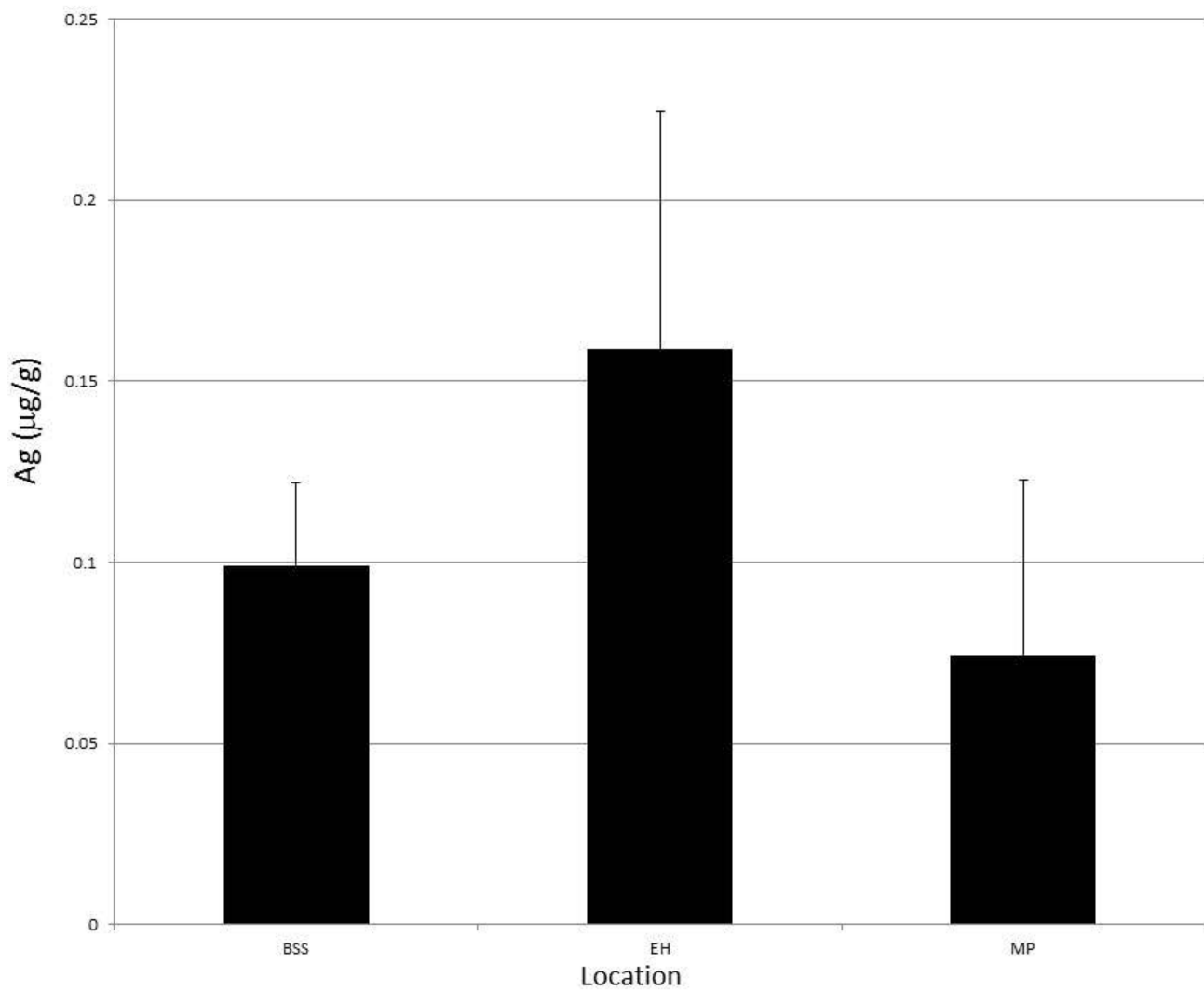


Figure 37: Silver (Ag) concentrations (µg/g). All samples were above the MDL.



## Thallium

**Background:** Thallium (Tl) is a soft silvery metal that tarnishes easily. It naturally occurs in the Earth's crust, as various ores, including pyrite. Thallium is also present in manganese nodules that occur on the ocean floor (RSC 2016n).

**Uses:** Thallium has limited uses due to its toxicity. It was historically used as a rodenticide, but this use has been discontinued in the United States as of 1965. Its most common current use is in photoelectric cells (RSC 2016n).

**Environmental effects:** Thallium has no known biological role. In aquatic environments, research has shown thallium to be toxic to algae, invertebrates and fish (Rickwood et al. 2015).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of thallium in Vieques ranged from 0.012 to 0.014  $\mu\text{g/g}$ , with a mean of 0.013  $\mu\text{g/g}$ . All samples were below the MDL, but because thallium is naturally occurring in the environment (i.e. unlikely to have a concentration of zero), samples with concentration below the MDL are reported as the MDL values.

**Spatial Patterns:** There are no statistically significant (Dunn's test,  $\alpha=0.05$ ) differences between the strata for thallium in conch.



Figure 39: Thallium (Tl) concentrations ( $\mu\text{g/g}$ ). All samples were below the MDL.

**Discussion:** Thallium was not quantified in queen conch in other studies in the region, so no comparison is possible. Based on the lack of a spatial pattern between the sampling areas, there is no evidence that thallium is elevated due to previous land uses, including military activities. Additional sampling, both for Vieques and elsewhere in the region, might provide more clarity as to whether if thallium might be elevated in queen conch in Vieques.

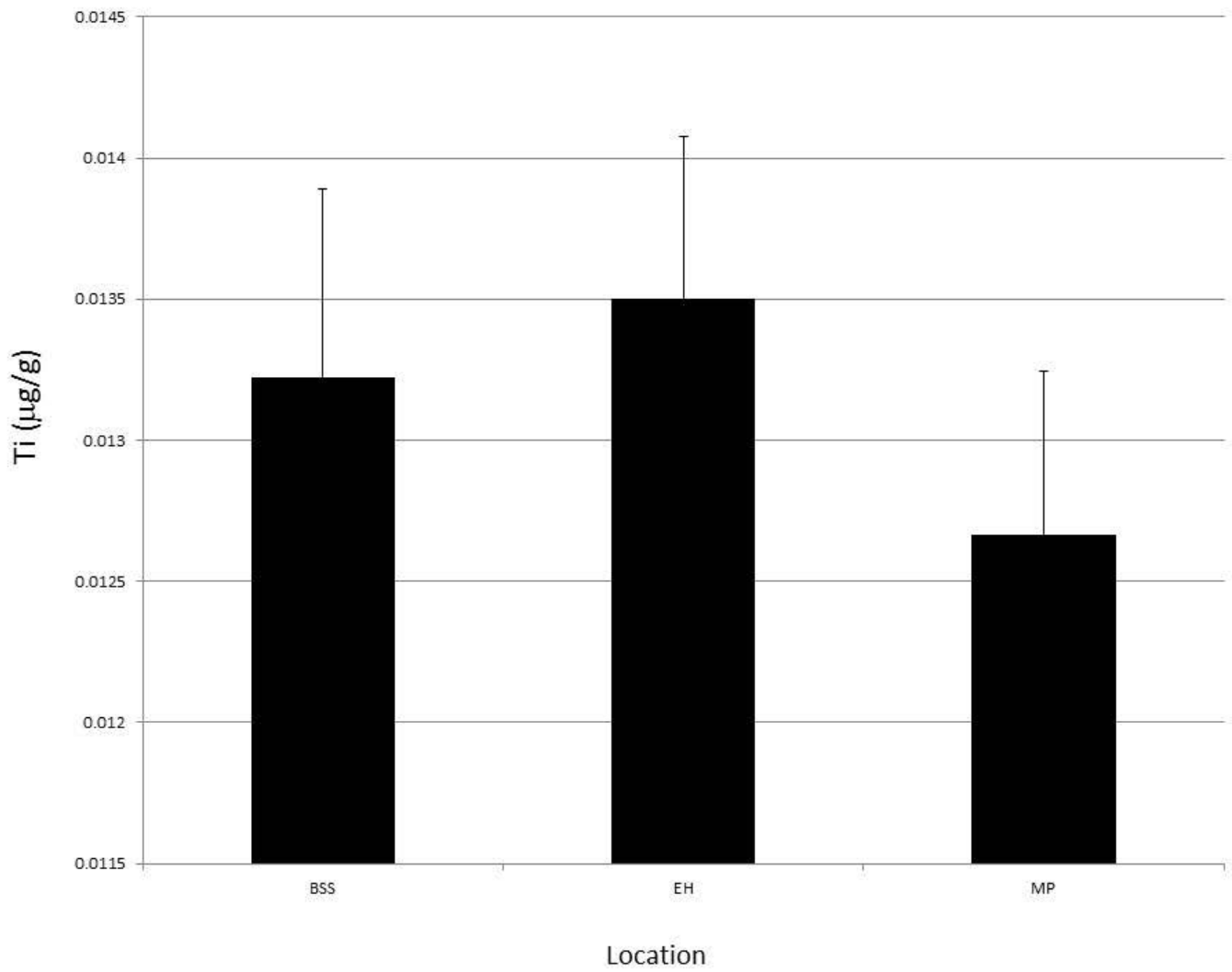


Figure 40: Thallium (Tl) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.

## Tin

**Background:** Tin (Sn) is a pliable metallic element that naturally occurs in the Earth's crust. It can exist as either as an inorganic or organic compound. Mining and use of tin has increased the amount of tin present in the environment.

**Uses:** Tin is used in metal coatings to prevent corrosion (e.g. tin-coated steel), a variety of alloys, window glass, fire retardants and in anti-foulant boat paints (RSC 2016o).

**Environmental effects:** Tin has no known biological role and the elemental metal is generally non-toxic. However, organic forms, especially butyltins used in boat paints, can be very toxic to marine organisms (RSC 2016o).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of tin in Vieques ranged from 0.020 to 0.042  $\mu\text{g/g}$ , with a mean of 0.034  $\mu\text{g/g}$ .



Figure 41: Tin (Sn) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Spatial Patterns:** There are no statistically significant (Dunn's test,  $\alpha=0.05$ ) differences between the strata for tin in queen conch.

**Discussion:** Tin concentrations in queen conch of Vieques were significantly lower (Wilcoxon test,  $\alpha=0.05$ ) than St. Thomas (Table 6). Based on this comparison and the lack of spatial differences within this study, it does not appear that historical land uses, including military activities, have impacted the levels of tin in queen conch tissues.

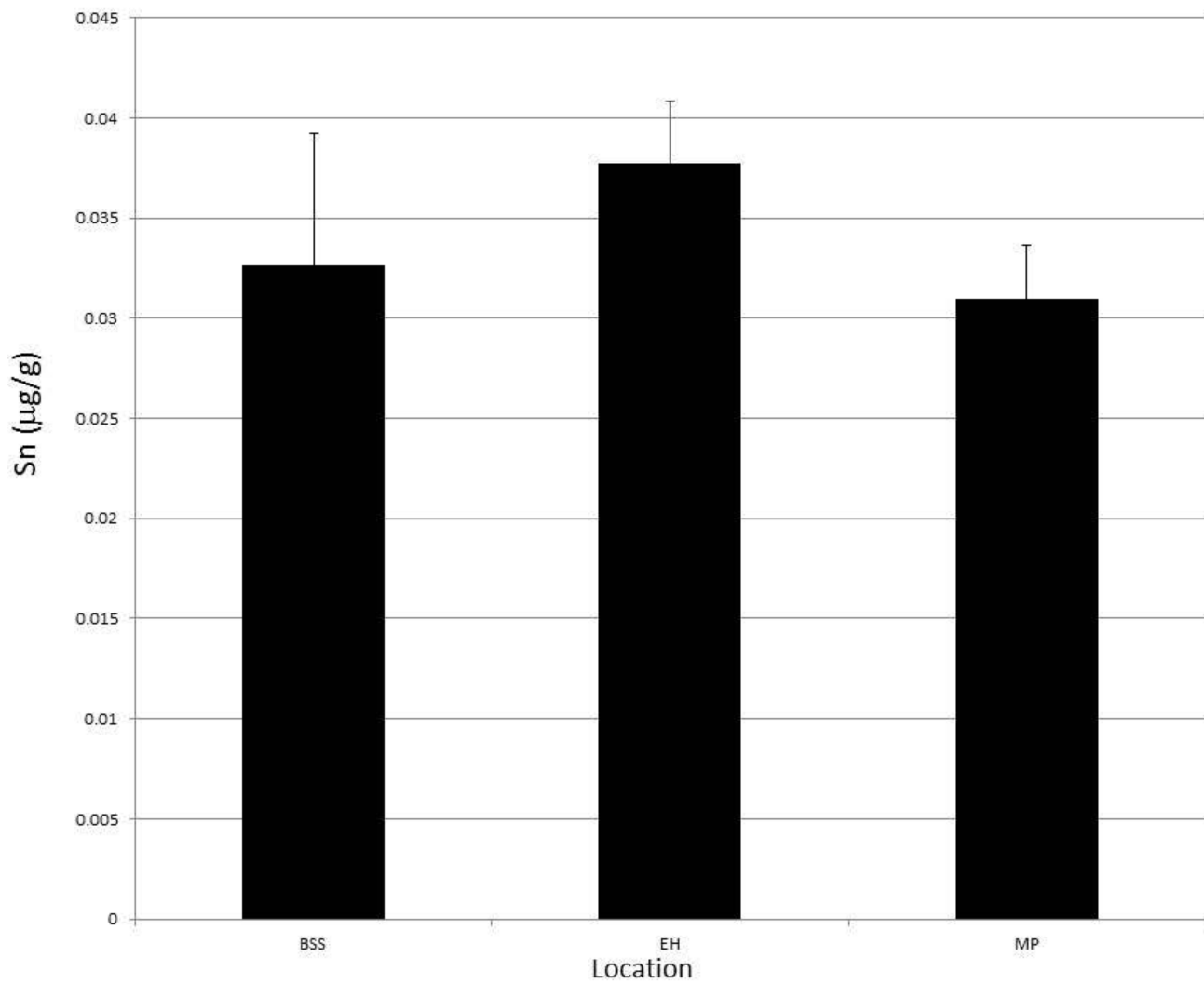


Figure 42: Tin (Sn) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Uranium

Background: Uranium (U) is a radioactive silvery metal that occurs naturally in the earth's crust.

Uses: Uranium is used in nuclear power generation, in nuclear submarines and in nuclear weapons (RSC 2016p). Depleted uranium is also used in ammunition; a limited number of depleted uranium shells were used in Vieques in 1999, but subsequent studies (ATSDR 2003; Pait et al. 2010) have not shown this to be of ecological or human health concern.

Environmental effects: Uranium has no biological role and is a toxic metal. In aquatic environments, uranium has been demonstrated to be toxic to a variety of organisms including invertebrates (Muscatello and Liber, 2009), fish and plants (CCME 2011).

Conch Tissue Concentrations in Vieques: Conch tissue concentrations of uranium in Vieques ranged from 0.136 to 0.827  $\mu\text{g/g}$ , with a mean of 0.491  $\mu\text{g/g}$ .

Spatial Patterns: Qualitatively, conch tissue concentrations for uranium in conch are higher on the eastern side of the island than at Mosquito Pier; however, these patterns were not statistically significant (Dunn's test,  $\alpha=0.05$ ).



Figure 43: Uranium (U) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

Discussion: Uranium was not quantified in queen conch in other studies in the region, so no comparison is possible. Based on the lack of a spatial pattern between the sampling areas, there is no evidence that uranium is elevated due to previous land uses, including military activities. Additional sampling, both for Vieques and elsewhere in the region, might provide more clarity as to whether uranium might be elevated in queen conch in Vieques.



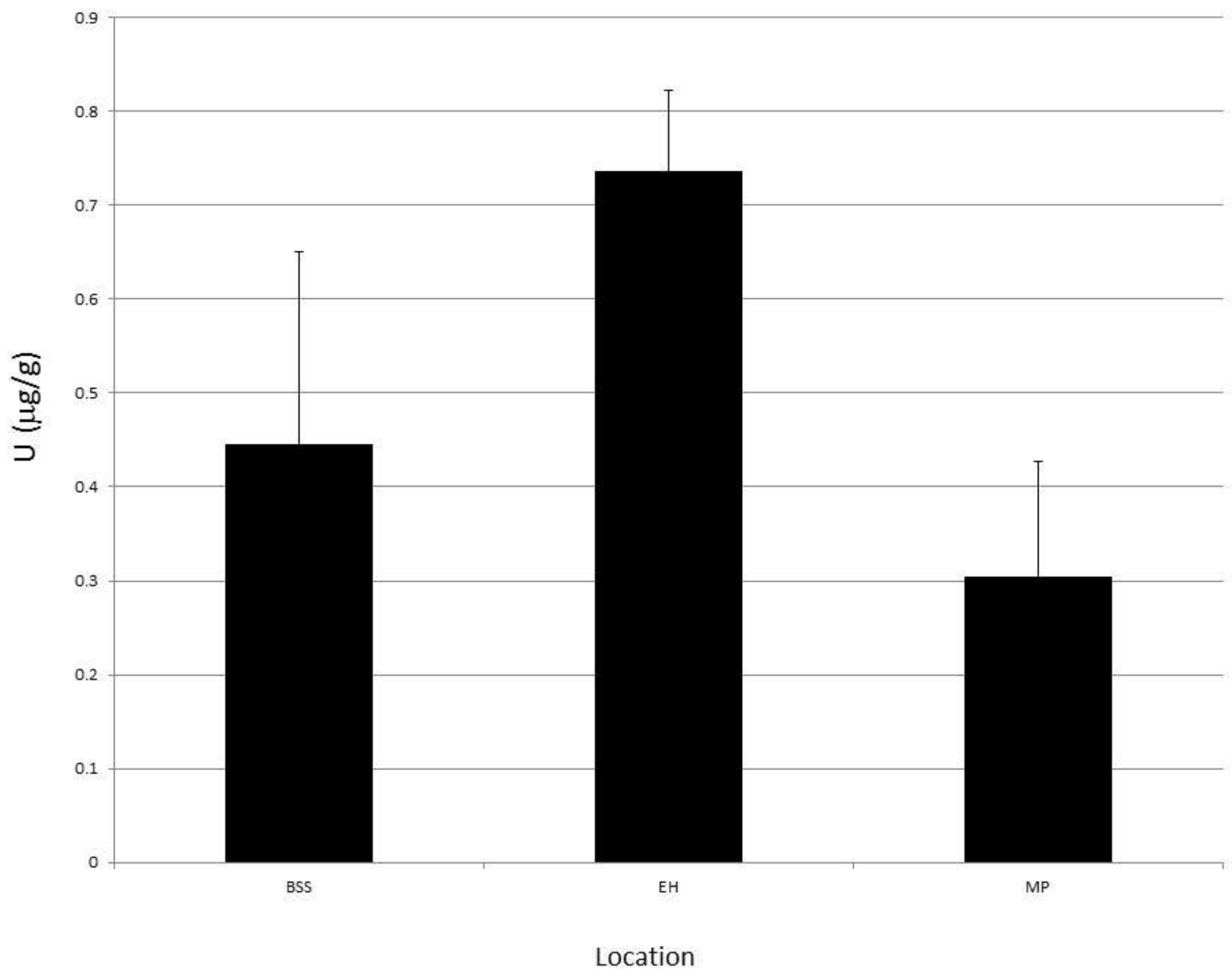


Figure 44: Uranium (U) concentrations ( $\mu\text{g/g}$ ) by strata. Error bars are one standard deviation.

## Vanadium

**Background:** Vanadium (V) is a silver corrosion resistant metal. It occurs naturally in the Earth's crust as a variety of minerals including phosphate rocks and iron ores. Mining and use of vanadium has increased the amount of vanadium present in the environment.

**Uses:** Vanadium is primarily used in steel alloys for such applications as armor plate, axles, tools, piston rods and crankshafts, in addition to use as a pigment in ceramics and glass (RSC 2016p). A common pathway for vanadium entering the environment is through the burning of fuel oil (Irwin 1997).

**Environmental effects:** Vanadium is a micronutrient for humans and some other animals, but is toxic at high concentrations. Vanadium toxicity increases as the valence state increases with pentavalent vanadium being the most toxic. Vanadium has been demonstrated to be toxic to fish (Sprague et al., 1978; Gravenmier et al., 2005), as well as invertebrates and plants (Irwin 1997).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of vanadium in Vieques ranged from 0.896  $\mu\text{g/g}$  to 5.53  $\mu\text{g/g}$ , with a mean of 2.87  $\mu\text{g/g}$ .

**Spatial Patterns:** Qualitatively, vanadium in queen conch is higher on the north side of the island (Mosquito Pier strata) than on the eastern side of the island, but this pattern is not statistically significant (Dunn's test,  $\alpha=0.05$ ).



Figure 45: Vanadium (V) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Discussion:** Vanadium was not quantified in queen conch in other studies in the region, so no comparison is possible. Based on the lack of a spatial pattern between the sampling areas, there is no evidence that vanadium is elevated due to previous land uses, including military activities. Additional sampling, both for Vieques and elsewhere in the region, might provide more clarity as to whether if vanadium might be elevated in queen conch in Vieques.

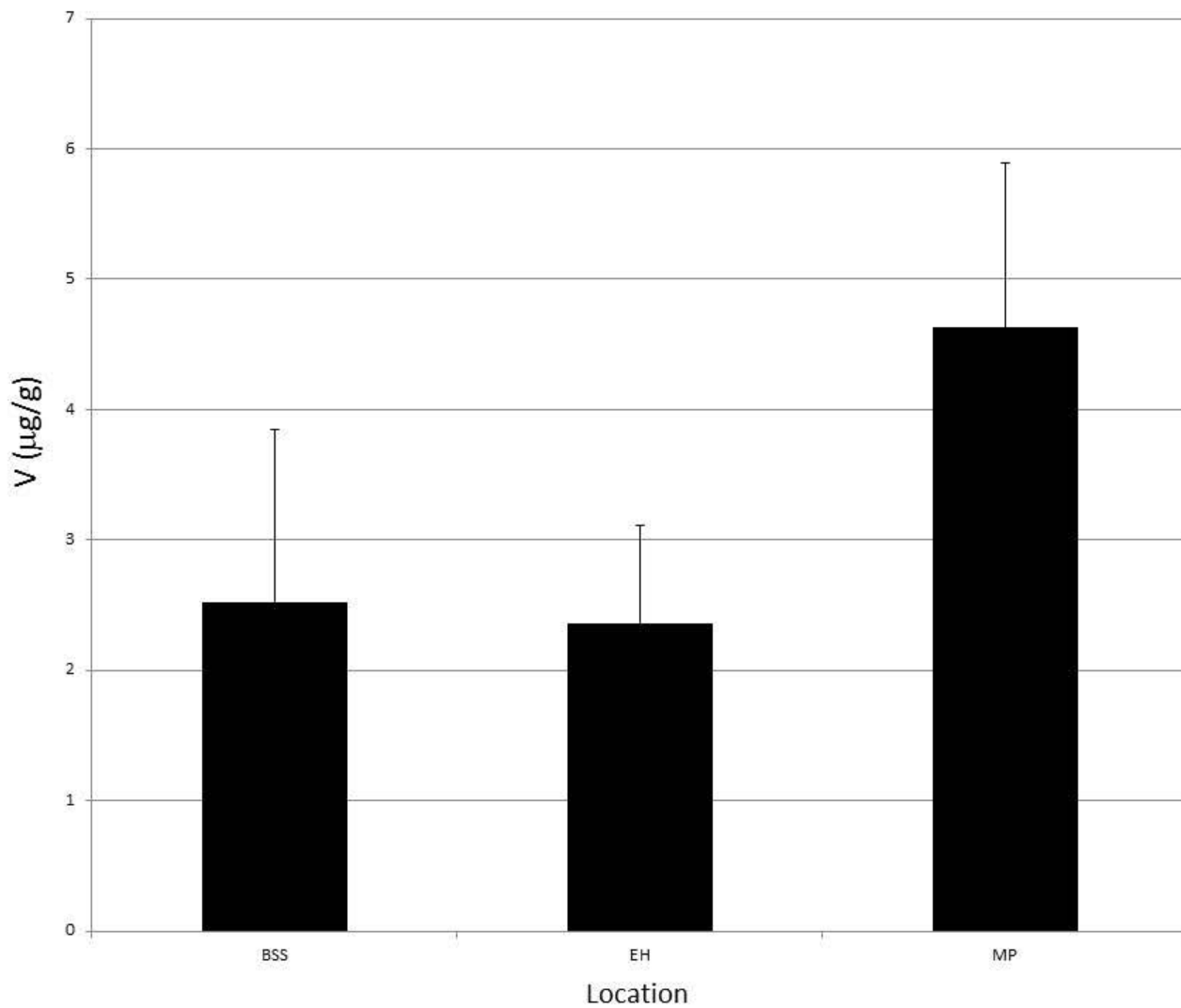


Figure 46: Vanadium (V) concentrations (µg/g) by strata. Error bars are one standard deviation.

## Zinc

**Background:** Zinc (Zn) is a metallic element that naturally occurs in the Earth's crust. Mining and use of zinc has increased the amount of zinc present in the environment.

**Uses:** Zinc is used in brass, bronze, die castings metal, alloys, rubbers, paints, wood preservation, catalysts, corrosion control in drinking water systems, photographic paper, vulcanization acceleration for rubber (including automobile tires), ceramics, textiles, fertilizers, pigments, batteries, and as nutritional supplements or medicines (EPA 2005).

**Environmental effects:** Zinc is a micronutrient for both plants and animals, but can be toxic in excess. Zinc has been shown to be toxic to aquatic invertebrates, including sea urchins (Novellini et al. 2003; Dermeche et al. 2012; Edullantes and Galapate, 2014), and fish (Besser and Lieb, 2007), but relative less toxic to mammals and birds (USDOI 1998). Zinc is most toxic to aquatic organisms at early life stages (USDOI 1998). Zinc accumulates primarily in the tissues of corals rather than the skeletons (Metian et al. 2014) and can cause reduction in fertilization success in scleractinian corals (Reichert-Brushett and Harrison, 2005).

**Conch Tissue Concentrations in Vieques:** Conch tissue concentrations of zinc in Vieques ranged from 7.51  $\mu\text{g/g}$  to 46.3  $\mu\text{g/g}$ , with a mean of 25.6  $\mu\text{g/g}$ .



Figure 47: Zinc (Zn) concentrations ( $\mu\text{g/g}$ ). All samples were above the MDL.

**Spatial Patterns:** Statistically, Bahia Salinas del Sur has higher zinc concentration in queen conch than Ensenada Honda (Dunn's test,  $\alpha=0.05$ ,  $p=0.040$ ).

**Discussion:** Qualitatively, zinc concentrations in queen conch of Vieques were higher than reported for Cuba, but lower than for Florida. Statistically, Vieques was significantly lower (Wilcoxon test,  $\alpha=0.05$ ) than St. Thomas (Table 6). Based on this comparison and the spatial differences within this study, it

does not appear that historical land uses, including military activities, have impacted the levels of zinc in queen conch tissues.

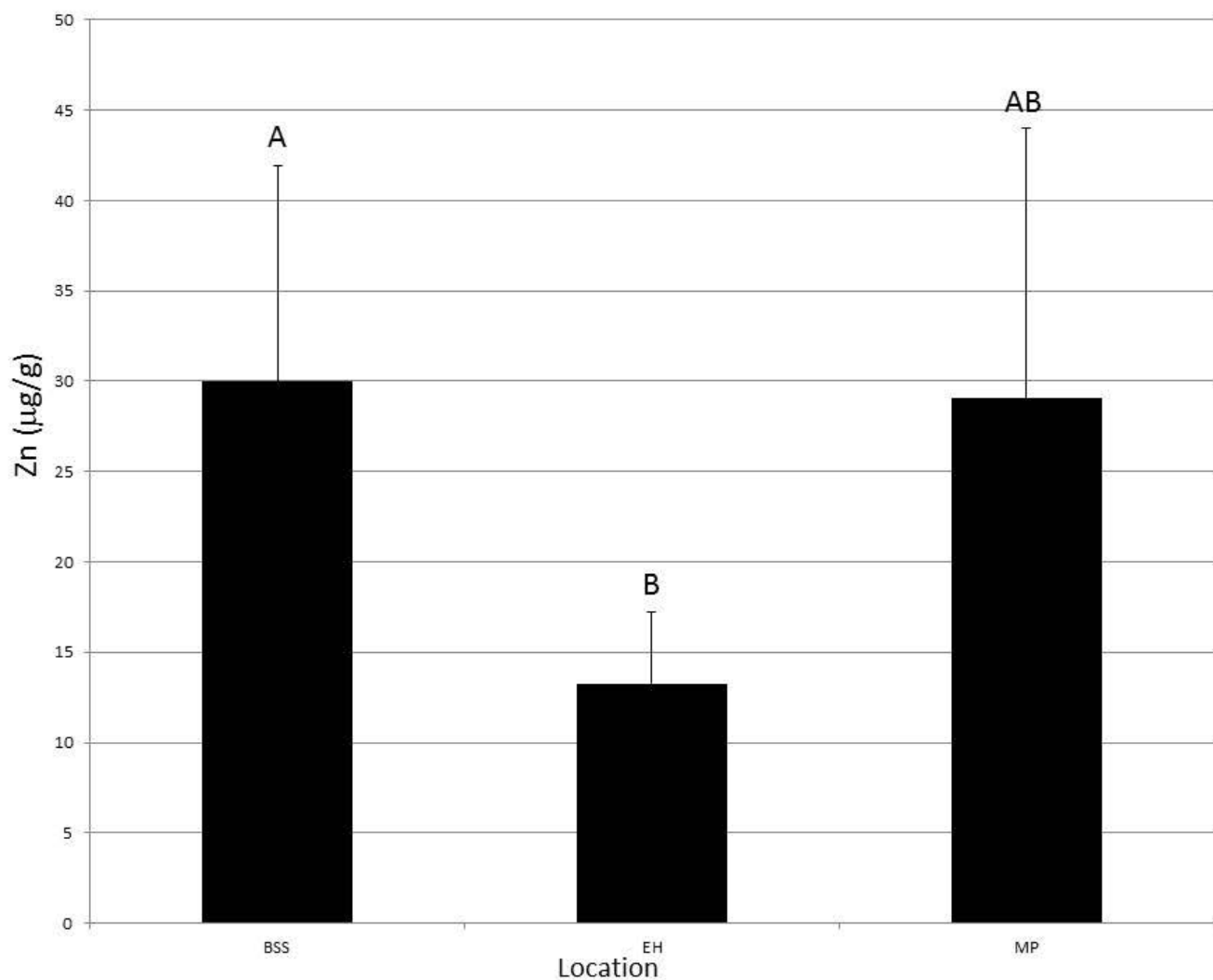


Figure 48: Zinc (Zn) concentrations (µg/g) by strata. Error bars are one standard deviation. Letter groupings show statistically significant differences between strata (Dunn's test  $\mu=0.05$ ).



## Conclusions

In general, the conch tissue data presented in this study fall within the range of reported values for the Caribbean. Exceptions to this pattern are Cr, Ni, and Se which were statistically higher in conch in Vieques than in the nearby St. Thomas East End Reserves (STEER) marine protected area. However, it should be noted that concentrations of Cu, Pb, Sn and Zn in the STEER exceeded those in Vieques. Furthermore, this study found that there was no clear “hot spot” of contamination between the three sampling areas in this study. Together, these two findings suggest that former land uses on Vieques, including military activities, have not resulted in unusually high contamination in conch.

In addition, no munitions compounds were found above the level of detection in any of the samples analyzed. Using very conservative seafood advisory guidelines, more than four servings of conch per month would exceed recommended levels of metal intake (arsenic and cadmium); however, using these same guidelines, other published concentration data suggest that conch from Cuba, Florida and St. Thomas also present risks at these consumption levels. As such, Vieques is not unusual for the region. Social science studies concerning the amount of seafood consumed by the residents of Vieques would allow for a more accurate assessment of seafood safety. The suite of chemical analyses employed in this study could be applied to additional species, including higher trophic levels which might be susceptible to bioaccumulation. It is recommended that future studies focus on species that are important both from an ecological and a fisheries perspective. Enhanced understanding of the extent and magnitude of contaminants in fisheries species allows for more holistic management and allows consumers to make informed dietary decisions.

## Acknowledgments

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**Table 1: Analytes quantified in queen conch and lobster tissues in this study.**

Munitions	Metals
1,3,5,7-tetranitro-1,3,5,7-tetrazocane	Aluminum
1,3,5-trinitroperhydro-1,3,5-triazine (RDX)	Antimony
tetryl	Arsenic
nitrobenzene	Barium
4-amino-2,6-dinitrotoluene	Beryllium
2-amino-4,6-dinitrotoluene	Cadmium
Trinitrotoluene (TNT)	Chromium
2-nitrotoluene	Cobalt
3-nitrotoluene	Copper
4-nitrotoluene	Iron
pentaerythritoltetranitrate	Lead
2,4-dinitrotoluene	Lithium
2,6-dinitrotoluene	Manganese
Azoxy ( 2,2',6,6'-Tetranitro-4,4'-azoxytoluene)	Mercury
	Nickel
DDT and breakdown products	Selenium
2,4'-DDD	Silver
2,4'-DDE	Thallium
Tin	
2,4'-DDT	Uranium
4,4'-DDD	Vanadium
4,4'-DDE	Zinc
4,4'-DDT	

**Table 2: Methodology, standards and range for munitions compound analysis.**

Analyte	ASE	Sonication	L C - M S / MS	GC/MS	I n t e r n a l Standard Used	Range (ng)
1 , 3 , 5 , 7 - t e t r a n i - tro-1,3,5,7-tetraazacyclooctane (HMX)	X		X		13C4, 15N4-HMX	10-250
1,3,5-trinitroperhydro-1,3,5-triazine (RDX)	X		X		13C3-RDX	10-250
Tetryl	X		X		13C7, 15N3-TNT	10-250
Nitrobenzene	X			X	d5-Nitrobenzene	50-250
2,4,6-trinitrotoluene		X	X		13C7, 15N3-TNT	10-250
4-Amino-2,6-dinitrotoluene		X	X		13C7, 15N3-TNT	10-250
2-Amino-2,4-dinitrotoluene		X	X		13C7, 15N3-TNT	10-250
2-Nitrotoluene	X			X	d5-Nitrobenzene	10-250
3-Nitrotoluene	X			X	d5-Nitrobenzene	10-250
4-Nitrotoluene	X			X	d5-Nitrobenzene	10-250
Pentaerythritol tetranitrate (PETN)	X		X		13C4, 15N4-HMX	10-250
2,4-dinitrotoluene	X			X	3,4-Dinitrotoluene	25-250
2,6-dinitrotoluene	X			X	3,4-Dinitrotoluene	25-250
2 , 2 ' 6 , 6 ' - t e t r a n i - tro-4,4'-azoxytoluene	X		X		13C4, 15N4-HMX	10-250



**Table 3: Summary statistics for total metals and total DDT in queen conch in Vieques. No mu-nitions compounds were detected. Values are wet weight as ng/g for DDT and µg/g for metals. Metal concentrations below the MDL are reported as the measured value, rather than zero.**

Analyte	min	max	mean	median
Ag	0.043	0.206	0.109	0.095
Al	13.1	61.2	33.725	28.35
As	4.18	20.2	9.504	8.655
Ba	0.036	0.285	0.180	0.178
Be	0.008	0.009	0.009	0.009
Cd	0.097	0.688	0.350	0.338
Co	0.03	0.045	0.033	0.032
Cr	0.948	2.08	1.449	1.365
Cu	4.77	26.3	11.25	9.435
Fe	59.5	197	128.031	116.5
Hg	0.017	0.045	0.028	0.023
Li	0.067	0.118	0.090	0.087
Mn	9.3	63.9	33.893	31.15
Ni	1.13	3.81	2.108	2.015
Pb	0.024	0.072	0.053	0.046
Sb	0.144	0.166	0.153	0.152
Se	0.492	0.967	0.652	0.604
Sn	0.02	0.042	0.034	0.035
Ti	0.012	0.014	0.013	0.013
U	0.136	0.827	0.492	0.470
V	0.896	5.53	2.877	2.45
Zn	7.51	46.3	25.632	20.3
Total DDT	0	0.195	0.013	0

**Table 4: Common uses and anthropogenic sources of metals (compiled from RSC 2015 and Eisler 1988).**

Metal	Symbol	Anthropogenic Uses and Sources
Aluminum	Al	Cans, foils, kitchen utensils, window frames, beer kegs, airplane parts. Also used in alloys with copper, manganese, magnesium and silicon
Antimony	Sb	Component in semi-conductors, and in alloys and compounds for batteries, bullets, cable sheathing, flame retardants, and enamels
Arsenic	As	Smelting, pesticides, herbicides, desiccants, wood treatments, agricultural growth stimulants (Eisler 1988).
Barium	Ba	Drilling fluids for oil and gas wells, paints, glass making, x-ray medicine, fire-works. Historically in rat poison.
Beryllium	Be	X-ray lithography, ceramic applications, alloys with copper or nickel to make gyroscopes, springs, electrical contacts, spot-welding electrodes and non-sparking tools, structural materials for high-speed aircraft, missiles, spacecraft and communication satellites
Cadmium	Cd	Batteries, pigments and in electroplating
Chromium	Cr	Leather tanning, stainless steel, metallic plating and in industrial catalysts
Cobalt	Co	Magnets, electroplating, paint, porcelain, glass, pottery and enamels.
Copper	Cu	Coins, wires, pipes, pesticides, industrial materials (e.g. heat exchangers), anti-fouling paints, alloys
Iron	Fe	Construction and manufacturing (steel, stainless steel and cast iron)
Lead	Pb	Car batteries, ammunition, weights (e.g. barbells and dive belts), crystal glass, solder and radiation protection. Historically, in pipes, pewter, paints, pottery glazes, insecticides, hair dyes, gasoline additives.
Lithium	Li	Pharmaceuticals, batteries, and in alloys for armor plating, aircraft, high speed trains and bicycles.
Manganese	Mn	A catalyst, rubber additive, in fertilizers, in pesticides, and in alloys with steel and aluminum.
Mercury	Hg	In the chemical industry as a catalyst, in some electrical switches. Historically, in manufacturing, batteries, fluorescent lights, dental fillings, felt production, thermometers.
Nickel	Ni	Batteries, coins, metal plating and a variety of alloys (e.g. stainless steel).
Selenium	Se	Glass production, fungicides, in photocells, solar cells, photocopiers and rectifiers
Silicon	Si	Semi-conductors (elemental Si), in construction (sand, clay and granite) and in alloys (used in machine tools, engine blocks and cylinder heads).
Silver	Ag	Jewelry, dental alloys, solder/brazing alloys, electrical contacts, batteries, circuits, photography and nanoparticles.
Thallium	Tl	Rodenticide (historically), photoelectric cells, low temperature thermometers and switches.
Tin	Sn	Anti-corrosion coatings (e.g. tin-coated steel), a variety of alloys, window glass, fire retardants and in anti-foulant boat paints
Uranium	U	Nuclear fuel and nuclear weapons.
Vanadium	V	Pigment for ceramics and glass, catalyst in magnet production, as an alloy with steel for armor plating, tools, pistons and crankshafts

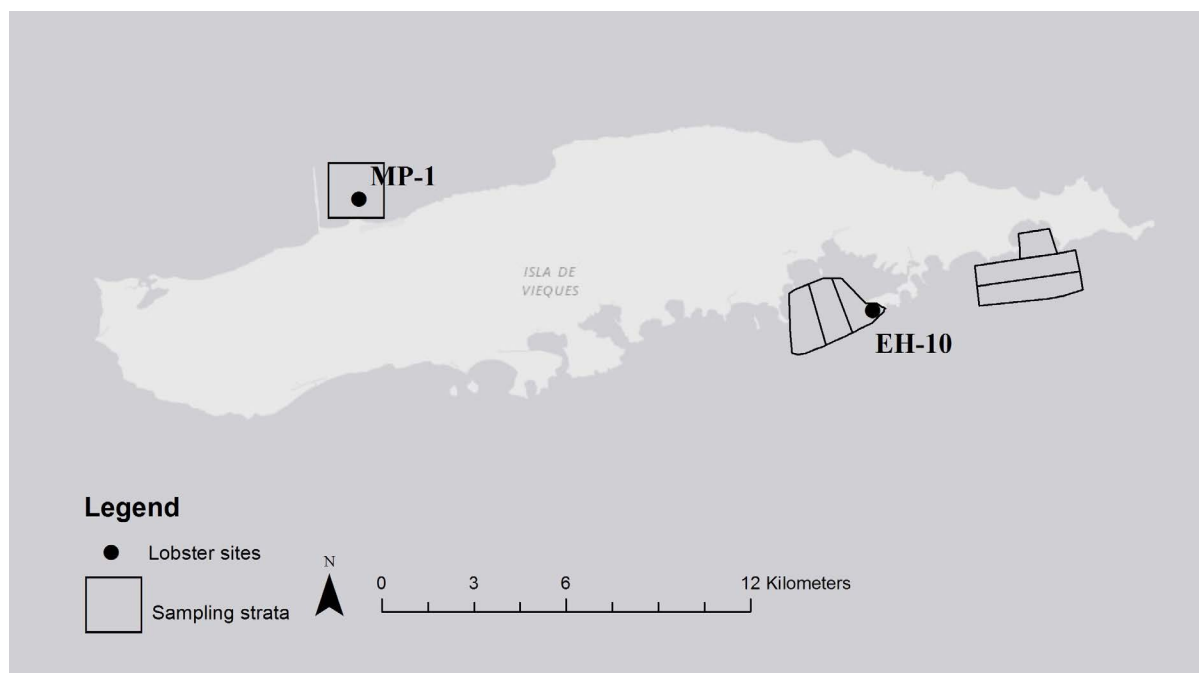
**Table 5: Comparison of data from queen conch in Vieques, Puerto Rico (this study) with US Environmental Protection Agency seafood consumption guidelines (USEPA 2000). EPA Guideline is based on sixteen 8 oz meals per month. Values are wet weight.**

	VQS	VQS	VQS	EPA
Analyte	max	mean	median	Guideline
Inorganic Arsenic (µg/g)	0.404	0.190	0.173	0.18
Cd (µg/g)	0.688	0.350	0.338	0.18
Hg (µg/g)	0.045	0.028	0.023	0.059
Se (µg/g)	0.967	0.652	0.604	2.9
DDT (µg/g)	0.195	0.013	0	29

**Table 6: Comparison of queen conch contaminant values from Vieques, Puerto Rico (this study) with queen conch data from Cuba (Rizo et al., 2010), St. Thomas, USVI (Apeti et al., 2014) and Florida (Glazer et al., 2008) Values are wet weight as ng/g for DDT and µg/g for metals.**

	Vieques	Vieques	Cuba	Cuba	St. Thomas	St. Thomas	Florida	Florida
Analyte	min	max	min	max	min	max	min	max
Ag	0.043	0.206	--	--	0.039	0.9	1.03	2.54
Al	13.1	61.2	--	--	10.164	191.268	--	--
Arsenic	4.18	20.2	--	--	4.319	13.085	--	--
Ba	0.036	0.285	--	--	--	--	--	--
Be	0.008	0.009	--	--	--	--	--	--
Cd	0.097	0.688	--	--	0.209	1.046	2.62	24.14
Co	0.03	0.045	--	--	--	--	--	--
Cr	0.948	2.08	--	--	0.345	1.295	--	--
Cu	4.77	26.3	6.4	32.6	10.044	28.798	14.06	84.34
Fe	59.5	197	--	--	74.976	353.43	--	--
Hg	0.017	0.045	--	--	0.0139	0.212	0.01	0
Li	0.067	0.118	--	--	--	--	--	--
Mn	9.3	63.9	--	--	10.622	84.49		
Ni	1.13	3.81	--	--	0.813	1.961	16.28	9.59
Pb	0.024	0.072	0.2	2.3	0.056	0.314	--	--
Sb	0.144	0.166	--	--	--	--	--	--
Se	0.492	0.967	--	--	0.117	0.571	--	--
Sn	0.02	0.042	--	--	0.010	3.353	--	--
Ti	0.012	0.014	--	--	--	--	--	--
U	0.136	0.827	--	--	--	--	--	--
V	0.896	5.53	--	--	--	--	--	--
Zn	7.51	46.3	20.4	31.1	27.918	326.43	30.53	660.32
DDT	0	0.195	--	--	0	0	2.02	7.57

## Appendix: Spiny Lobster Results and Discussion



*Figure A1: Lobster sampling sites (n=2).*

Figure A1 shows the locations of the two spiny lobsters caught during the 2014 field mission. Only three lobsters were observed during the sampling week, one of which escaped capture. Because of the small sample size, great care should be taken in interpreting these data. These data are presented here in interest of transparency and completeness, but more lobster data would be required to effectively evaluate contamination in lobster tissue in Vieques. No munitions were detected in lobster tissues. DDT, nor its degradation products, were detected in lobster tissues. Table A1 shows the raw data for the two lobster sites. Table A2 compares data from this study with the very conservative EPA seafood safety guidelines (EPA 2000).

**Table A1: Concentrations in lobster tissues. All values are on a dry weight basis. Metals are µg/g. DDT is ng/g and is the sum of the parent compound (DDT) and its degradation products.**

Analyte	EH-10	MP-1
Ag	0.053	0.057
Al	8.87	9.95
As	22.7	24.5
Ba	0	0
Be	0	0
Cd	0.100	0
Co	0	0
Cr	0.489	0.456
Cu	10.6	10.6
Fe	11.6	11.6
Hg	0.027	0.026
Li	0.075	0.067
Mn	0.130	0.153
Ni	0.111	0
Pb	0	0
Sb	0	0
Se	0.348	0.344
Sn	0	0
Tl	0	0
U	0	0
V	0.19	0.175
Zn	16.6	21.6
DDT	0	0

**Table A2: Comparison of lobster tissue contaminants data to EPA seafood guidelines (EPA 2000).**

Analyte	EH-10	MP-1	EPA Guideline
Inorganic Arsenic (g/g)	0.454	0.49	0.18
Cd (µg/g)	0.100	0	0.18
Hg (µg/g)	0.027	0.026	0.059
Se (µg/g)	0.348	0.344	2.9
DDT (µg/g)	0	0	29







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NOAA TECHNICAL MEMORANDUM NOS NCCOS XX CHEMICAL CONTAMINANTS IN THE MARINE RESOURCES OF VIEQUES, PUERTO RICO